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U. S. DEPARTMENT OF AGRICULTURE

DIVISION OF CHEMISTRY

BULLETIN No. 28

PROCEEDINGS

OF THE

SEVENTH ANNUAL CONVENTION

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

HELD AT

THE U. S. NATIONAL MUSEUM AUGUST 28, 29, AND 30, 1890

METHODS OF ANALYSIS OF COMMERCIAL FERTILIZERS, FOODS AND FEEDING STUFFS, DAIRY PRODUCTS, FERMENTED LIQUORS, AND SUGARS

EDITED BY

HARVEY W. WILEY

SECRETARY OF THE ASSOCIATION

PUBLISHED BY AUTHORITY OF THE SECRETARY OF AGRICULTURE

WASHINGTON

GOVERNMENT PRINTING OFFICE

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LETTER OF TRANSMITTAL.

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
Washington, D. C., November 26, 1890.

SIR: I have the honor to submit the report of the Proceedings of the Seventh Annual Convention of the Association of Official Agricultural Chemists, with the recommendation that it be published as heretofore as a bulletin of the Chemical Division of the Department.

Respectfully,

H. W. WILEY,
Chemist.

Hon. J. M. RUSK,
Secretary of Agriculture.

PROCEEDINGS OF THE SEVENTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, HELD AT WASHINGTON, AUGUST 28, 29, AND 30, 1890.

FIRST DAY.

MORNING SESSION, THURSDAY.

In accordance with the call of the executive committee, the association met in the lecture hall of the U. S. National Museum at 10 o'clock, the president, Mr. M. A. Scovell, in the chair.

The following members and "others interested in the objects of the association" were present:

Hon. Edwin Willits, Assistant Secretary of Agriculture.

The president, Mr. M. A. Scovell, director of the Kentucky Agricultural Experiment Station, Lexington, Ky.

The vice-president, Mr. G. C. Caldwell, chemist of the New York Agricultural Experiment Station, Ithaca, N. Y.

The secretary, Mr. H. W. Wiley, chief chemist, U. S. Department of Agriculture.

Of the executive committee, Mr. J. A. Myers, of Morgantown, W. Va.; and the following members and participants:

Allen, E. W., Washington, D. C.
Alvord, Henry E., Agricultural College, Md.
Anderson, J. T., Auburn, Ala.
Atwater, W. O., Washington, D. C.
Battle, H. B., Raleigh, N. C.
Bowman, Walker, Blacksburg, Va.
Burney, W. B., Columbia, S. C.
Carpenter, F. B., Raleigh, N. C.
Cooke, W. W., Burlington, Vt.
Crampton, C. A., Washington, D. C.
Dancy, F. B., Raleigh, N. C.
De Ghequier, A., Washington, D. C.
Edson, Hubert, Patterson, La
Farrington, Edward H., Champaign, Ill.
Frear, William, State College, Pa.
Gaines, Richard H., Richmond, Va.
Gascoyne, W. J., Baltimore, Md.
Gibson, Charles B., Chicago, Ill.
Harris, A. W., Washington, D. C.
Herff, B. v., Washington, D. C.
Horton, Horace E. L., Washington, D. C.
Huston, H. A., Lafayette, Ind.
Kedzie, R. C., Lansing, Mich.
Knorr, Aug. E., Washington, D. C.
Lupton, N. T., Auburn, Ala.
McBryde, J. B., Columbia, S. C.
McDonnell, H. B, State College, Pa.
Nicholson, H. H., Lincoln, Nebr.
Parsons, Charles L., Hanover, N. H.
Patterson, H. J., Agricultural College, Md.
Patterson, L. G., Agricultural College, Miss.
Penny, C. L., Newark, Del.

Richards, Edgar, Washington, D. C.
Richardson, Clifford, Washington, D. C.
Robinson, Norman, Tallahassee, Fla.
Ross, B. B., Baton Rouge, La.
Schweinitz, E. A. v., Washington, D. C.
Shiver, Frank S., Columbia, S. C.
Street, J. P., New Brunswick, N. J.
Stubbs, William C., Audubon Park, New Orleans, La.
Terne, Bruno, Philadelphia, Pa.
Trescot, T. C., Washington, D. C.
Van Slyke, L. L., Geneva, N. Y.
Voorhees, E. B., New Brunswick, N. J.
Whitney, Milton, Columbia. S. C.
Williams, William J., Philadelphia, Pa.
Woods, Charles D., Middletown, Conn.

ADDRESS OF MR. M. A. SCOVELL, PRESIDENT

The president called the convention to order, and spoke as follows:

GENTLEMEN OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS: We begin to-day the seventh annual meeting of this association. In opening the meeting I take pleasure and feel justified in congratulating you upon the progress made by the association in this brief period, and the manifest influence it is exerting in making comparable the results in the chemical analyses of fertilizers and agricultural products in general.

The proceedings of this association have always been carefully edited and only what we considered valuable put into our publications. Its progress, therefore, is shown in the statement that the proceedings of the second annual convention covered fifty pages of printed matter, the third sixty, the fourth eighty, the fifth ninety-six, and the sixth two hundred and thirty-six pages.

When the association was first organized the primary object of it, as stated in the constitution, was to secure uniformity and accuracy in the methods and results of fertilizer analysis. At that time it was considered a gigantic undertaking, and it was not considered feasible to take up other subjects of investigation. The first two or three years were taken up with potash and phosphoric acid alone. As late as 1885 we find Wiley describing the use of the Gooch crucible in potash determinations. We found that a uniform method of determining nitrogen was so great a task that up to 1886 the committee on nitrogen had no report to make, but now we have methods not only for determining nitrogen, potash, and phosphoric acid, but we have been enabled to expand by taking up the subjects of cattle foods, the analysis of sugar, and dairy products, and have set a committee to work on the methods of analysis of fermented liquors.

This rapid progress has been accomplished by being thoroughly organized and having so many active workers in our ranks, thus being enabled to test methods by many actual trials in a single year and further to note the error of personal influence which is ever present and which should have its bearing in the adoption of methods. I think its greatest influence has been felt by reason of our careful selection of methods and still more careful changes in them, and for always demanding the results, not only of the individual, but of the several

members, to substantiate the accuracy of any method or any change of method before adoption. That our methods are adopted by agricultural chemists generally in this country is seen by all, almost all published results stating that the methods used were those adopted by the Association of Official Agricultural Chemists. Abroad we have found our methods published in several journals, and they have been incorporated in Griffith's book on Commercial Fertilizers, published in England.

During the meeting of the Association of Agricultural Colleges and Experiment Stations last November it was recommended that all analyses made at experiment stations be made by the methods adopted by the Association of Official Agricultural Chemists, and that if any chemist saw reason for following other methods it should be distinctly so stated wherever the results were published.

That such an organization, probably the strongest in the country, should adopt such a resolution shows the influence exerted by this association.

Thus it will be seen that our methods have been recommended to be adopted by over forty stations in this country. The analytical work to be done by these stations is simply enormous, and as these results as they will accumulate and multiply will either assist in greatly advancing our knowledge of agricultural science or retarding it, we should feel the responsibility resting upon us. This should lead us to carefully consider all changes in methods, and yet be ever ready to make changes where we find weak points in them, wherever we can simplify the work, and wherever we can shorten it with due regard to accuracy. To this end I desire to call the attention of the association to a few things which I believe require careful consideration by you.

RECOMMENDATIONS.

First is the matter of a standard acid solution. On the accuracy of determining this depends the results of our nitrogen, whether in commercial fertilizers, cattle foods, or other products. This point heretofore has not been neglected by the association, as we have adopted four different ways of determining the strength of the acid solution. But I am decidedly of the opinion that in many instances the variation of our results is not so much the fault of the methods in determining nitrogen as in the varying strength of the acid used by the different analysts. My attention was called to this last year by a comparison of the acids used by the various chemists who reported on nitrogen determinations. This year further investigations have led me to have made a series of trials to test the strength of the acids by the various methods now in use by the association. Prof. A. M. Peter carefully determined our standard acid by the various ways with the following results:

By precipitating the chlorine and weighing the silver chloride according to Crooke's method, he found that one liter of one-tenth normal

ammonia, which should contain 1.400 grams nitrogen if the standard were exactly one-tenth normal, did actually contain 1.406 grams nitrogen. This result was obtained from the mean of three closely agreeing determinations.

The potassium tetra-oxalate method gave 1.418 grams nitrogen to the liter and by distilling ammonium chloride 1.423 grams nitrogen were obtained.

Upon the distillation of ammonio-ferrous sulphate 1.414 grams, and by the distillation of ammonium iron alum 1.416 grams were obtained.

At first sight these results would seem close enough for practical use. But let us see the results of the various factors on No. 1 nitrogen samples sent out this year; .7 gram used. It will be seen from these results that the standard acid alone, if made by the various methods, is responsible for the discrepancy of .12 of 1 per cent. It seems to me, therefore, that it is again worth while to call the attention of the association to the preparation of a standard acid and to take steps by means of which the standard acids of the various laboratories may become absolutely comparable.

It is time that the ammonium citrate-soluble phosphoric acid should receive serious consideration by this association. The method as it stands is open to many objections. It is in regard to this subject that our veracity as chemists is often questioned, and when this is done we can say but little in our own behalf for a method that on the slightest provocation will give results in duplicate varying from 1 to 3 per cent.

A few minutes under or over the regulation half hour will often play havoc with us. A thermometer whose veracity is not up to the standard will often cause us much anxiety when we come to compare our results. A slight acid or alkaline tendency of the solution, too delicate perhaps to be noticed by litmus or coralline, is no doubt the cause of many of the attacks of our fertilizer friends. There is now beginning to be used in this country a considerable amount of hydrated aluminum phosphate in our commercial fertilizers. This seems to be much more soluble in a slightly alkaline solution of ammonium citrate than in a slightly acid solution.

Dr. Gibson, of Chicago, sends me some very interesting results which relate directly to this question. The continuous dissolving action of neutral ammonium citrate solution is well known. His experiments would tend to show that when the solution was slightly alkaline the dissolving action ceased at a given point, supposed by Dr. Gibson to be reached whenever the available P_2O_5 is dissolved. His results on South Carolina rock, dissolved by ammonium citrate solution, by the official method, gave 1.01, .90, .83; an average of .913. By the ammonium citrate solution, slightly alkaline, .75, .73, .76; mean .746. By digesting for one hour, official method, 1.85, 1.83, 1.86; mean, 1.846. Slightly alkaline ammonium citrate solution, .787, .740, .760; mean, .761.

On aluminic phosphate by official method 19.80, 19.90, 19.63; mean 19.77. Ammonium citrate solution, slightly alkaline, 31.24, 33.44, 30.31, mean 31.66. By digesting 1 gram for one hour instead of one-half hour, as required by the official method, the results were: in neutral citrate solution, 31.48, 32.11, 30.59, mean 31.39; in slightly alkaline citrate solution, 34.68, 34.79, 34.73; mean 34.73; thus indicating by the remarkable agreeing results with the alkaline solution that the dissolving action had ceased, while a variation of 2 per cent in the neutral solution would indicate the opposite.

Since receiving Dr. Gibson's results we have started some experiments on a similar line. They are not yet completed, but some of the results are out. On the same sample we get by the official method 18.61 per cent available P_2O_5; by adding 1 cubic centimeter of 10 per cent ammonia to 100 cubic centimeters of the neutral citrate ammonia solution, and using this in place of the official solution, we obtained 25.32 available P_2O_5. Certainly by concerted action the association might throw much light on this subject during the year. According to all preconceived ideas aluminum phosphate should be available to plants, and we should hesitate to continue a method of analysis, without thorough investigation, which gives less than one-half of the phosphoric acid as being available.

The question of the division of cattle foods should, I believe, receive the careful consideration of this association. Mr. Wiley called attention last year to the fact that it was impossible to analyze grains by the method as adopted. This is self-evident to all those who have such work to do. I would suggest, therefore, that the subject of cattle foods be divided into fodder analysis and grain analysis.

Ash analysis is an important subject and one that must necessarily receive the attention of experiment stations. If the experiment stations are to look to us for methods we should begin at once to systematize a method for ash analysis. This would probably require the appointment of another reporter.

The work of the individual members analyzing the uniform samples sent out by the various reporters has been the chief cause of our progress and success. Nothing should be done to discourage this important feature of our work, but as the association continues to take up new subjects for investigation the time will soon come, if not already at hand, when it will be too much of a task for each member to analyze all the samples. I believe the tendency is for the members to select too many subjects and not give enough attention to duplication or investigating new methods. Some plan by which it would be the duty of the members, grouped into divisions, to take up special work would, I believe, be feasible and successful.

In conclusion allow me to state, in the words of my predecessor, that the aim of this society is "to lay a foundation so solid that every court in this land must respect its conclusions, and every analytical chemist,

whether he lives in this country or elsewhere, must be forced either to practice or admit the advantages and correctness of our system of analyses. Step by step we have advanced through the difficult problems before us, feeling that we have steadily gained ground and that we are molding public sentiment in a manner that must redound to the advantage of the whole country and secure the highest respect for the science to which we are devoting our lives."

Mr. Wiley presented the following report of the executive committee on order of business:

PROGRAMME.

HOURS OF MEETING.—Morning hours, 9.30 to 12.30; afternoons, at 2.

1. Report on Determination of Nitrogen, by Mr. E. B. Voorhees.
2. Report on Analysis of Dairy Products, by Mr. E. H. Jenkins.
3. Report on Analysis of Potash, by Mr. N. T. Lupton.
4. Report on Analysis of Cattle Foods, by Mr. G. C. Caldwell.
5. Report of Committee on Foods and Feeding Stuffs.
6. Report on Analysis of Sugars, by Mr. H. W. Wiley.
7. Business meeting; election of officers, etc.
8. Report on Analysis of Phosphoric Acid, by W. B. Burney.
9. Report of Committee on National Chemical Society.
10. Report on Analysis of Fermented Liquors, by Mr. W. B. Rising.

The committee recommends that immediately following the reading of each report any written communications relating to the subject of such report shall be presented and read, the discussion upon the report to be deferred until such papers, if any, have been submitted to the association.

The committee announces that through the courtesy of the Assistant Secretary of Agriculture the services of Mr. Talma Drew, who made the stenographic report of the proceedings last year and aided the secretary in the preparation of the bulletin, have again been secured.

M. A. SCOVELL.
G. C. CALDWELL.
H. W. WILEY.
J. A. MYERS.

Mr. Myers moved that the report be accepted, and that the programme and recommendation therein contained be adopted. Carried.

Mr. Wiley stated that he had a letter from Mr. E. H. Jenkins, reporter on analysis of dairy products, inclosing his report, which would be read by the secretary when reached in the order of business. Mr. Jenkins was ill and could not attend the meeting. Mr. W. B. Rising, reporter on analysis of fermented liquors, had supposed that the meeting would be held in September, as it was last year. In connection with the preparation of his report he made a special trip to Europe, and had just sailed from Liverpool on his return. He had forwarded a partial report, and the work would be completed in time for publication in the bulletin.

Mr. Wiley announced that the committee on arrangements had made provision for an excursion on the following evening down the Potomac to Marshall Hall, where an excellent dinner would be served for the members and friends of the association.

The president suggested that it would be well to invite the Secretary and Assistant Secretary of Agriculture to attend the convention and address the members of the association.

Mr. Frear moved that a committee be appointed to extend the invitation of the association to Hon. J. M. Rusk, Secretary of Agriculture, and Hon. Edwin Willits, Assistant Secretary of Agriculture, to be present at the meeting. Carried; and the president appointed as such committee Messrs. Frear, Kedzie, and Caldwell.

Mr. Voorhees presented the following report:

REPORT ON DETERMINATION OF NITROGEN.

By E. B. Voorhees.

As your reporter on nitrogen, I now have the honor to present the results of the work done by the association this year. As far as your reporter has been able to review the foreign and American journals he has not found that the past year has developed any particularly new or desirable additions to our present official methods. The report, therefore, will include chiefly (1) the results secured by members of the association, and (2) recommendations and suggestions.

Early in the year a circular letter asking coöperation in the work of the association was sent to all chemists connected with Experiment Stations, to seven commercial chemists, and to such others as were so entitled by our constitution, numbering in all about forty. Thirty-two, representing twenty-six stations, the United States Department of Agriculture, and that of Virginia, and five commercial chemists, signified their desire to take part in the work. Three samples were sent to each of these early in March, accompanied by another circular letter, asking that a moisture determination be made in each of the samples, and that the nitrogen determination be made according to the official and alternate methods. The report for 1889 had not then been distributed, hence they were asked to use those methods described in the report of the association for 1888, with such additional modifications as were recommended by the reporter in 1889. The samples were marked 1, 2, and 3, and were made up as follows:

Description of samples.	Per cent nitrogen.	Grams.
No. 1:		
Potassium nitrate, containing	13.72	400
Sodium nitrate, containing	16.14	56
Calculated per cent of nitrogen	14.01	
No. 2:		
Linseed meal, containing	7.15	250
Cotton-seed meal, containing	5.50	250
Sodium nitrate, containing	16.14	100
Calculated per cent of nitrogen	7.96	
No 3:		
Dried blood, containing	13.92	300
Ammonite, containing	13.02	300
Calculated per cent of nitrogen	13.47	

The report includes the work of twenty-four chemists, representing but fourteen of the twenty-five Experiment Stations which early in the season desired to coöperate, and the Departments of Agriculture of the United States and of Virginia. No commercial chemists are represented.

RESULTS.

The percentage of moisture was not reported by all of the chemists, and since the amounts reported in samples 1 and 3 were very uniform, all results are based upon original substance. The method of standardizing the acid was mentioned in only three reports; in these the tetra-oxalate was used with good results.

KJELDAHL MODIFIED FOR NITRATES.

Analysts.	Per cent nitrogen.	
	No. 1.	No. 2.
Walker Bowman (Virginia Experiment Station)	13.95	7.49
R. C. Kedzie (Michigan Experiment Station)	14.04	8.40
H. R. Baldwin (West Virginia Experiment Station)	13.73	7.88
F. B. Carpenter (North Carolina Experiment Station)	13.76	7.36
H. J. Patterson (Maryland Experiment Station)	13.82	7.66
B. F. Finney (Virginia Experiment Station)	13.86	7.77
R. H. Gaines (Virginia Department of Agriculture)	14.13	7.68
T. C. Trescot (United States Department of Agriculture)	13.40	7.65
J. M. Bartlett (Maine Experiment Station)	14.12	7.64
L. H. Merrill (Maine Experiment Station)	14.20	7.74
W. H. Beal (Massachusetts Experiment Station)	13.80	7.61
F. W. Morse (New Hampshire Experiment Station)	14.13	8.04
C. L. Parsons (New Hampshire Experiment Station)	14.05	7.79
C. D. Woods (Storrs Experiment Station)	14.04	7.97
Duncan Adriance (Texas Experiment Station)	13.79	
A. L. Winton and R. S. Curtis (Connecticut Experiment Station)	13.74	7.74
L. A. Voorhees and C. S. Cathcart (New Jersey Experiment Station)	14.04	7.94
B. B. Ross (Louisiana Experiment Station)	14.11	7.87
G. L. Holter (Pennsylvania Experiment Station)	13.45	7.81
M. A. Scovell (Kentucky Experiment Station)	14.08	7.99
A. M. Peter (Kentucky Experiment Station)	14.02	8.03
H. E. Curtis (Kentucky Experiment Station)	13.99	7.93
Average of whole number	13.91	7.80
Average of twenty	13.96	7.81

KJELDAHL METHOD.

Analysts.	Per cent nitrogen.
	No. 3.
Walker Bowman (Virginia Experiment Station)	13.35
R. C. Kedzie (Michigan Agricultural College Experiment Station)	13.72
H. R. Baldwin (West Virginia Experiment Station)	13.45
F. B. Carpenter (North Carolina Experiment Station)	13.40
H. J. Patterson (Maryland Experiment Station)	13.55
B. F. Finney (Virginia Experiment Station)	13.72
R. H. Gaines (Virginia Department of Agriculture)	13.77
T. C. Trescot (United States Department of Agriculture)	13.16
J. M. Bartlett (Maine Experiment Station)	13.54
L. H. Merrill (Maine Experiment Station)	13.63
W. H. Beal (Massachusetts Experiment Station)	13.26
F. W. Morse (New Hampshire Experiment Station)	13.31
C. L. Parsons (New Hampshire Experiment Station)	13.46
C. D. Woods (Storrs Experiment Station)	13.49
Duncan Adriance (Texas Experiment Station)	13.07
A. L. Winton and R. S. Curtis (Connecticut Experiment Station)	13.43
L. A. Voorhees and C. S. Cathcart (New Jersey Experiment Station)	13.46
B. B. Ross (Louisiana Experiment Station)	13.71
G. L. Holter (Pennsylvania Experiment Station)	13.08
M. A. Scovell (Kentucky Experiment Station)	13.63
A. M. Peter (Kentucky Experiment Station)	13.53
H. E. Curtis (Kentucky Experiment Station)	13.49
Average	13.46

RUFFLE METHOD.

Analysts.	Per cent nitrogen.		
	No. 1.	No. 2.	No. 3.
F. B. Carpenter (North Carolina Experiment Station)	13.49	7.41	13.39
H. J. Patterson (Maryland Experiment Station)	13.72	7.70	13.71
T. C. Trescot (United States Department of Agriculture)	13.82	7.75	13.55
W. H. Beal (Massachusetts Experiment Station)	13.84	7.62	13.28
G. L. Holter (Pennsylvania Experiment Station)	13.30	7.80	.....
Average	13.63	7.66	13.48

SODA-LIME METHOD.

Analysts.	Per cent nitrogen.
	No. 3.
H. J. Patterson (Maryland Experiment Station)	13.73
H. E. L. Horton (United States Department of Agriculture)	13.46
W. H. Beal (Massachusetts Experiment Station)	13.29
C. D. Woods (Storrs Experiment Station)	13.56
New Jersey Experiment Station	13.44
G. L. Holter (Pennsylvania Experiment Station)	13.30
Average	13.46

ABSOLUTE METHOD.

Analysts.	Per cent nitrogen.	
	No. 1.	No. 2.
T. C. Trescot (United States Department of Agriculture)	13.77	7.79
A. L. Winton and R. S. Curtis (Connecticut Experiment Station)	.....	7.67

TABLE OF AVERAGES.

Method.	Number of sample.	Number of analysts.	Per cent nitrogen.			
			Average.	Highest.	Lowest.	Difference.
Kjeldahl	3	22	13.46	13.77	13.07	0.70
Kjeldahl modified for nitrates	1	22	13.91	14.20	13.40	0.80
	2	21	7.81	8.40	7.36	1.04
Ruffle	1	5	13.63	13.84	13.30	0.54
	2	5	7.66	7.80	7.41	0.39
	3	4	13.48	13.71	13.28	0.43
Soda-lime	3	6	13.46	13.73	13.29	0.44

All of the chemists represented reported results by the official methods; those reported by the alternate are in addition to the official.

KJELDAHL MODIFIED FOR NITRATES.

Remarks.—The average of the results reported on sample No. 1 is 13.91; excluding two that report much less nitrogen than the sample is shown to contain, the average is 13.96, or .05 of 1 per cent less than the calculated percentage.

On a basis of an average of 13.96 per cent, nine chemists are within one-tenth of 1 per cent, the limit usually allowed for experimental error; thirteen chemists, or 65 per cent of the whole number, are within .15 of 1 per cent, the limit often allowed between duplicates; 20 chemists, or the whole number included in the average, are within .3 of 1 per cent, the limit of error allowed by commercial chemists for what is termed "factory work."

The average of the results on sample No. 2 is 7.81; if we exclude one which is evidently much too high, and one too low, the average remains the same, and is .15 of 1 per cent less than the calculated percentage. Eight chemists are within .1 of 1 per cent of either the calculated per cent of 7.96, or the average per cent secured of 7.81. Taking .2 of 1 per cent as the limit of error, eleven chemists are within the same on the basis of the calculated per cent, while on the basis of the average secured sixteen are within the limit. Inasmuch as more than half the whole number of results reported on this sample are lower than the average of 7.81, the result above noted would seem to indicate either that the calculated per cent was too high, or that on a mixture of this character the results secured by the official method are too low. While sample No. 2 is an unusual mixture and somewhat difficult to manage, I am of the opinion that the trouble is not with the method.

If we simply compare the average of this year with that of last year, the results by the modified Kjeldahl show no apparent improvement, yet the fact that the average this year represents the work of twenty-four experiment station chemists, some of whom are reported to be inexperienced, as against fifteen chemists last year, which number included commercial chemists of high standing, it indicates a slight improvement in the work, and seems to me to fully verify the statement made by Mr. Scovell, in his report for 1889, viz, "that the modified Kjeldahl method is an accurate and reliable one for the determination of nitrogen in fertilizers containing nitrates."

KJELDAHL METHOD.

The average of the determination reported on sample No. 3 is practically identical with the calculated percentage. Ten chemists are within .1 of 1 per cent of the average, and the difference between the highest and the lowest is but .43 of 1 per cent, a result which is highly satisfactory.

ALTERNATE METHODS.

The results on Nos. 1 and 2, by both the "Ruffle" and absolute methods, are lower than by the official, though a fair comparison can not be made, owing to the very few reports by these methods. The soda-lime method gave results practically identical with those secured by Kjeldahl.

In accordance with the recommendations made by the reporter in 1889 the chemists of the Kentucky Station reported results secured on official samples Nos. 1 and 2 by substituting for two grams of zinc dust and two grams of salicylic acid, 2 grams of zinc sulphide and 1 gram of salicylic acid.

Results.

Analysts.	Per cent. nitrogen.		
	No. 1.	No. 2.	Potassium nitrate, C. P.
M. A. Scovell	14.08	7.99	.....
A. M. Peters	.....	7.82	13.79
H. E. Curtis	13.99	7.76	.....
Theoretical	14.01	7.96	13.83
Average association results	13.96	7.81	.....

The above results are the averages of several determinations agreeing closely with each other.

A practical test of this method was also made at the New Jersey Station, where thirty-three samples of commercial fertilizers containing nitrate nitrogen, ranging from .1 to 2.62 per cent, were duplicated by the official Kjeldahl for samples containing nitrates and by the suggested modification.

2 grams salicylic acid and 2 grams zinc dust.	1 gram salicylic acid and 2 grams zinc sulphide.	2 grams salicylic acid and 2 grams zinc dust.	1 gram salicylic acid and 2 grams zinc sulphide.	2 grams salicylic acid and 2 grams zinc dust.	1 gram salicylic acid and 2 grams zinc sulphide.
3.51	3.63	4.96	4.94	3.31	3.31
3.51	3.59	3.03	2.99	1.32	1.24
2.53	2.50	2.69	2.70	1.25	1.31
4.21	4.24	4.21	4.26	2.82	2.78
4.36	4.32	4.06	4.07	3.16	3.04
3.03	2.91	1.90	1.88	2.80	2.74
3.97	4.03	3.22	3.31	2.41	2.38
2.69	2.78	1.85	1.83	4.56	4.56
2.22	2.17	4.12	4.99	3.42	3.34
3.03	3.00	1.10	1.06	3.18	3.30
4.55	4.56	1.45	1.39	3.13	3.08
3.54	3.62	2.91	2.85	.....	.....

The results were highly satisfactory. The difference in duplicates ranged from nothing to .12 of 1 per cent, with an average difference on the whole number of .02 of 1 per cent.

ERRORS DUE TO REAGENTS.

A few chemists reported difficulty in securing uniform results on sample No. 1 when different weights were used and the proper deduction made for error due to reagents. This is an important point and should be carefully noted in the study of methods. Mr. Woods, of the Storrs Station, says that "Kjeldahl modified has in blank determinations always given some nitrogen. Should not be surprised at this if it were not that we always obtained about the correct percentage of nitrogen in nitrates (pure salts) without the use of the correction thus obtained, and the results have always been too low when the correction has been used." His report on this point is of considerable value and is appended in full.

MODIFIED KJELDAHL METHOD.

Mean of four "blanks" gave nitrogen corresponding to .4 cubic centimeters of ammonia solution, equal to .0012 gram nitrogen.

With potassium nitrate (theory), 13.84 per cent; mean by Tiemann-Schultze method, 13.75 per cent nitrogen.

Per cent nitrogen.	
Without correction.	With correction.
13.75	
13.78	
13.76	
13.68	
Av. 13.74	13.27

Nitrogen in samples.

[Percentages calculated on water content at receipt.]

No. 1.

Per cent nitrogen.		
Siemann—Schultze method.	Modified Kjeldahl.	
	Without correction.	With correction.
14.03	14.05	
14.08	14.01	
14.16	14.06	
14.19		
Av. 14.09	14.04	13.57

No. 2.

Modified Kjeldahl method.	
Without correction.	With correction.
P. ct. N.	*P. ct. N.*
7.92	
8.02	
7.96	
7.98	
8.00	
Av. 7.97	7.85

The work of Mr. Woods verifies the experience of the New Jersey Station, where the error due to reagents had previously been shown to be equivalent to .0010 gram nitrogen, and which had produced widely varying results on pure nitrates when the proper deduction had been made for different weights taken, the results being invariably from .2 to .5 of 1 per cent low when less than half a gram of the material was taken. The following determinations on sample No. 1 were made to illustrate this point.

Weight taken.	Without correction.	With correction.
Gram.	*Per cent.*	*Per cent.*
.9	13.93	13.82
.8	14.05	13.92
.7	14.12	13.98
.5	14.06	13.86
.5	14.04	13.84
.5	14.11	13.91
.4	14.04	13.79
Average..	14.05	13.87

The average of the four determinations on one-half gram or less, without correction, is 14.05; with correction it is 13.85, or .20 of 1 per cent less; the average of the three without correction on more than one-half gram taken is 14.03; with correction 13.91, or .12 less.

It seemed reasonable to infer from this work that the results secured without the deduction for error were nearer to the truth and hence they have been used in the report rather than the others. Further blank determinations were made with proper precautions at our station and it was shown that our assumed error was too great, since the variations in the results ranged from an equivalent of .0002 gram nitrogen to .0010 gram; in all cases within the limit of experimental error.

RECOMMENDATIONS.

I would recommend that the present official methods be continued for the coming year, but modified to include the use of 2 grams of zinc sulphide and 1 gram salicylic acid, instead of the 2 grams zinc dust and 2 grams salicylic acid, where duplicate determinations of nitrogen are made in fertilizers containing nitrates. My reasons for this are as follows:

(1) The results reported by this method are quite as satisfactory as by the official method.

(2) The zinc sulphide can all be added at once, and is, therefore, much less troublesome than the zinc dust.

(3) The oxidation is more rapid, and, owing to the fact that less salts are present, the distillation is more quiet,

SUGGESTIONS.

I would suggest, not as an improvement of the official methods, but in order to facilitate work and save expense: (1) That the digestion and distillation be performed in the same flask; (2) that metallic mercury be used instead of the mercuric oxide.

I would also suggest that the importance of the work of the association demands that the chemists coöperating should give it their best attention. It is not work that should be left until there is nothing else to do. And I would further suggest that the work of the reporter is largely a work of love, and he should receive the results at least one week before the annual convention.

The secretary stated that no written communications relative to the determination of nitrogen had been handed in, and the president announced that discussion upon the report was in order.

Mr. Huston said that, while he did not in the least question the value of the report, he desired to state that out of five hundred samples in his office not one contained nitrogen equal in amount to the least quantity determined in the samples sent out; moreover the mixtures were quite different, only one of the five hundred samples referred to containing nitrates. He realized that much of the difficulty experienced was due to nitrates, but it seemed to him that none of the samples represented the run of the work which fell to the lot of chemists west of the Alleghany Mountains, and he thought it proper that this matter should be taken into consideration when the next set of samples was sent out. His principal work was still upon raw bone, which was troublesome.

Mr. Wiley said that the mixtures of sample No. 1 were potassium nitrate and sodium nitrate, and he believed that the calculated percentage of nitrogen present in the mixture had been stated by Mr. Voorhees as 14.01 per cent. He would ask whether Mr. Voorhees had examined the two constituents of this mixture and was absolutely certain that they contained the full theoretical amount of nitrogen.

Mr. Voorhees said that the samples were very finely ground and thoroughly mixed; in making his own determinations they were mixed again. The percentage of nitrogen found in the potassium and sodium nitrate used formed the basis for calculating the amount that should be present in a uniform mixture of the two salts in the proportions indicated. In about ten analyses made before the samples were sent out the results were practically uniform, and the average was quite near the calculated percentage. The results reported to him indicated that the sample was thoroughly mixed. He had no other basis upon which to make his calculation, and had not supposed it impossible to make a thorough mixture of such materials when thoroughly pulverized.

Mr. Ross inquired whether Mr. Voorhees had tried the use of sodium hypophosphite, suggested by Mr. Burney last year.

Mr. Voorhees said that he had not.

Mr. Ross said that in several determinations he had used sodium hypophosphite instead of zinc dust, but in some cases had been so unfortunate as to lose portions of the solution, and had worked out but

one or two determinations. Sample No. 1 had given 13.99 per cent, which seemed rather low as compared with his other results; it now appeared, however, to be nearer the theoretical result than 14.11 per cent, which he secured by the regular method. In his opinion digestion took place much more rapidly than when zinc dust was used, and after the potassium permanganate was added, and the solution had cooled, it showed less tendency to cake, dissolved much more readily, and consequently gave a solution which required less dilution than when zinc dust was employed.

The president said that exact figures should be handed to the secretary for publication; oral reports could not be accepted.

Mr. Ross said that he had secured 13.86 per cent on sample of potassium nitrate. He could only report single determinations on potassium nitrate and on sample No. 1. He did not desire to state them as official, but merely gave them for what they were worth.

Mr. Van Slyke called attention to a method that was merely mentioned in the report made by Mr. Scovell last year (p. 85), being the method of J. W. Gunning, described in the Zeitschrift für Analytische Chemie, vol. 28, pp. 188–191, in which the author used one part potassium sulphate and two parts strong sulphuric acid. He (Mr. Van Slyke) could not now present figures, but wished to say that during the year he had used the method referred to a good deal with wheat middlings, flour, and various organic substances for the special purpose of comparison with the regular official method, and had found that the results by Gunning's method agreed as closely as did the duplicates by the official method. Dr Morse, of Johns Hopkins University, had used the Gunning method in his laboratory for the past year in determining nitrogen in a large variety of organic compounds, and with very satisfactory results. The advantage of this mixture was in its great simplicity; only the potassium sulphate and strong sulphuric acid were used, the oxidation took place quietly and with comparative rapidity, and a perfectly clear mixture was made; no potassium permanganate or other oxidizing mixture whatever had to be added. The solution was very clear, and in the speaker's experience had always distilled without bumping, some special precautions being taken in that regard. By this method the accumulation of reagents was avoided, which was always a desirable object. He hoped that the method might be tested on the samples sent out this year.

Mr. Myers inquired whether Mr. Van Slyke had tried the method on bone meal.

Mr. Van Slyke said that he had not.

The president said that he had tried it with the pure nitrates of different kinds in the samples, and invariably lost nitrogen by driving off ammonium sulphate. He had made some experiments. It worked well with the cattle foods, but in large quantities the contents of the flask got solid and hard, so that he supposed ammonium sulphate went off.

Mr. Van Slyke said that in that case he used more sulphuric acid.

The president said that if too much were used the oxidation would not take place; the other method seemed simpler.

Mr. Van Slyke said that the method in the form stated was not intended to apply to nitrates.

The president said that his own remarks referred simply to nitrogen in the organic form.

Mr. Cooke said that he had used the Gunning method on perhaps fifty samples of milk nitrogens, and finally abandoned it because of the length of time required to complete the digestion, which he thought would average nearly twice as long as that of the official method. The results obtained were very good.

Mr. Voorhees said that he would like to hear from those members of the association who had used zinc sulphide instead of the zinc dust.

The president said that he used it in his laboratory.

Mr. Voorhees said that the reporter had forgotten that the use of zinc sulphide had been recommended by the reporter of last year, and since the report of the last convention had not appeared when his samples were sent out, it had not been included in his recommendation to the chemists taking part. He would like to have an expression of the opinions of those who had used it.

Mr. Farrington said that his results had been good. In the dried blood samples more even results were obtained by grinding finely. He wished to know whether, in the determination of nitrogen by the Kjeldahl method, as modified by Scovell, the reagents were to be added in any particular order—whether the chemists added the substance to the acid or the acid to the substance.

Mr. Voorhees said that the method required the addition of the acid to the substance; that was the method as published, and he had always followed the direction. His custom was to add to the substance the metallic mercury, then the mixture of sulphuric and salicylic acids, then the zinc sulphide; then came the digestion.

The president said that he had followed that method in former years, but found the results less accurate than those obtained when the sulphuric acid was added to the substance. In regard to the zinc sulphide he thought the results very remarkable. The sulphide could be thrown in and the work started; the oxidation would proceed very rapidly and the duplicates would compare better than those with zinc. There was liability to loss when zinc was added; it would flash up. He made his own zinc sulphide, but blackjack might be used.

Mr. Voorhees inquired whether, in the digestion of pure nitrates (sample No. 1), difficulty had been experienced in getting a perfectly colorless product. He had found that even when a colorless liquid was obtained there was still a crystallization which remained dark for some time. He had not found that the dark color made any difference in the results, but wondered what it meant, whether there was lack of oxidation, or some combination formed there which crystallized in that color.

Was the oxidation really complete when one got a colorless liquid, or was it necessary to continue until a perfectly colorless product was obtained?

The president said that he had not observed it.

Mr. Voorhees said that with the zinc sulphide added he had no trouble whatever; he got a colorless product in a short time, and the results were equally good.

The president said that on a trial of that method he obtained his results in thirty-five minutes.

Mr. Woods asked whether any member of the association had experimented in the determination of nitrogen by the Kjeldahl method, plain or modified, in samples of soils, say 10, 20, or 50 grams. This was a matter in which he was interested, and he had not met with much success.

Mr. Huston said that he had used the Kjeldahl method with peats and with some of the so-called "bogus" soils of Indiana, but these were so high in nitrogen that he had taken only a little material to work with. In that line the method had been very successful with him, but perhaps his conditions were not the same as those of Mr. Woods. For a year he had used a special flask to save transferring, and found a great advantage in that.

Mr. Woods said that for 100 grams of soil he used a flask four or five times the size of the ordinary Kjeldahl flask, but in his laboratory different results were obtained according as 5, 10, 20, 50, or 100 grams were analyzed; the more he used the lower were his results.

The president asked Mr. Woods if he preserved the proportion of acid in analyzing the various amounts.

Mr. Woods said that he did, and that if there were errors from excess of acid the resulting percentages ought to be larger rather than smaller.

The president said that it would be well to remember such suggestions as were made by the members of the association in the course of discussion, and to give them a trial in making the analyses for the ensuing year. It was desired to get the best and shortest methods possible. The reporter's recommendations were now in order.

Mr. Wiley stated his desire that each reporter should send to him, as secretary, the full method upon his subject, as the same should be modified and adopted in this convention. It would be easy to do this by cutting the pages embracing the subjects in the bulletin of last year and erasing and inserting matter, as might be required by the modifications agreed upon. Each reporter was responsible for his own report in the forthcoming bulletin.

Mr. Voorhees said that he had made but one recommendation, as follows:

I would recommend that the present official methods be continued for the coming year, but modified to include the use of 2 grams of zinc sulphide and 1 gram salicylic acid, instead of the 2 grams zinc dust and 2 grams salicylic acid, where duplicate

determinations of nitrogen are made in fertilizers containing nitrates. My reasons for this are as follows:

(1) The results reported by this method are quite as satisfactory as by the official method.

(2) The zinc sulphide can all be added at once, and is therefore much less troublesome than the zinc dust.

(3) The oxidation is more rapid, and owing to the fact that less salts are present the distillation is more quiet.

Continuing, Mr. Voorhees said that he did not recommend this method as one to be used exclusively, but thought that in the case of fertilizers containing nitrates it worked better.

Mr. Cooke asked whether the change indicated was the substitution of the figure 1 for the figure 2 in the last line on page 220.

The president replied that the change recommended was as stated by Mr. Cooke, with the further substitution of zinc sulphide for zinc dust.

Mr. Cooke asked whether the word "*gradually*," in line 1 on page 221, was to be retained or omitted.

The president said that it might be left out; the zinc sulphide could be thrown in if desired; it made no disturbance.

Mr. LUPTON. I would suggest that we put in there what we have here, and say *or* zinc sulphide.

The PRESIDENT. The amendment suggested is that we use the old method or 1 gram of salicylic acid and 2 grams zinc sulphide, in which case the zinc sulphide can be put in at once.

Mr. Voorhees accepted the amendment, and his recommendation as modified thereby was adopted.

Mr. Voorhees stated that, in addition to the recommendation, which had been passed upon, he had made some suggestions, at the end of his report, as follows:

I would suggest, not as an improvement of the official methods, but in order to facilitate work and save expense: (1) That the digestion and distillation be performed in the same flask: (2) that metallic mercury be used instead of the mercuric oxide.

I would also suggest that the importance of the work of the association demands that the chemists coöperating should give it their best attention. It is not work that should be left until there is nothing else to do. And I would further suggest that the work of the reporter is largely a work of love, and he should receive the results at least one week before the annual convention.

The president said that the suggestions would be considered one at a time.

Mr. Voorhees said, in regard to the first suggestion, that he had found the rapidity of the work very materially increased by digesting and distilling in the same flask, and that a flask thus used would last quite as long as one used for either digestion or distillation alone. Being asked whether his flasks were made to order, he said that he had had them made specially but did not now; he thought it paid to have them made to order according to one's own idea. He had ordered them made somewhat thicker than usual. The flask he used was of about 500

cubic centimeters, and made in form of the ordinary 500 cubic centimeter flask, except that the bottom was round instead of flat; when made to order he had them made of rather heavy Bohemian glass, with the necks a little longer and more pear-shaped than those of the ordinary 500 cubic centimeter flask. He used a rose burner in which the holes were drilled at an angle of about 65°. The digestion was much more rapid than in the ordinary long-necked Kjeldahl flask, and a great deal of time was thus saved. In the digestion of some samples containing nitrates there was a bumping or something which checked the flask, but this was no more serious in a flask used for distillation alone than in one used for both digestion and distillation. The ordinary flask could be used but four, five, or six times.

The President said that he understood Mr. Voorhees's suggestion to be only a suggestion, not to be put to vote.

Mr. Voorhees said that the suggestion was made to be thought about by the members of the association. It did not alter the method or detract from its value and accuracy to use one flask instead of two; the suggestion was merely as to the saving of time. It was in the same line with the use of metallic mercury, which was easier to handle and gave a better oxidation than mercuric oxide.

Mr. Kedzie said that the modified form of flask referred to had been used in his laboratory and was found convenient and satisfactory; he would recommend it to any one who had not tried it, and thought that those who used it once would continue to do so.

Mr. Huston said that he had used a special flask like that described by Mr. Voorhees, a round-bottom 500 cubic centimeter flask, with a neck large enough to carry a No. 7 rubber stopper. At first he had expected to experience difficulty by reason of the material splashing on the sides and being hard to remove, and one of his assistants tried to see whether he could heat the acid enough to bring down all the solid matter even if it was carried far up in the neck. He found he could heat it so high that the drops of acid condensing in the neck would be carried within an inch of the top of the flask without any appreciable loss of nitrogen in the flask. He had never experienced any loss of nitrogen, and the many tests made had given good results.

Mr. Farrington said that he had used the flasks spoken of, and thought it would be wise to adopt them, the only objection being that they broke very easily.

Mr. Van Slyke said that by using a small glass funnel in a wide-mouthed flask, with a watch crystal over the mouth of the funnel, there would be no loss, and the acid would condense at a lower temperature and wash down the side very satisfactorily.

The president said that the question was on the adoption of the methods as amended.

Mr. Myers stated that the method adopted last year required the use of .7 gram of mercuric oxide. He thought that if the use of metallic

mercury were made an alternate method it should be incorporated at that point by inserting the words *or its equivalent in metallic mercury.*

The president said that he found a little nitrogen in mercuric oxide, and therefore thought that metallic mercury was better.

Mr. McDonnell asked whether the mercuric oxide was to be weighed each time. The direction was "approximately .7 gram," and he had always used a little scoop which held approximately that quantity.

The president said that he used a little stopcock with a slight depression in one side, so that every time it was turned it gave just so much. This had been suggested by some German chemist.

Mr. Kedzie moved that the amendment suggested by Mr. Myers be adopted. Carried.

Mr. Patterson asked whether the method, as it now stood, required the use of 1 gram of salicylic acid with the zinc sulphide and 2 grams with the zinc dust.

The president said that it did; 2 grams had to be used with zinc.

Mr. Patterson said that as he understood the amendment the two methods were now made into one, so that the amendment as it stood would have to be changed.

The president said that Mr. Patterson was mistaken; the insertion of the word *or* as suggested by Mr. Myers and moved by Mr. Kedzie, had set the matter right.

Mr. Ross referred to the matter of bumping in distillation, and stated that the method directed the addition of granulated zinc or pumice stone. For the past few months he had simply added one-half a gram of zinc dust immediately before the addition of the sodium hydrate, had experienced no trouble by bumping, and had not broken a flask or checked the bottom of one in the last forty or fifty distillations. The same plan had been tried at the Alabama Station, where it had worked very satisfactorily.

The president said that he saw an objection to this in that nearly all sodium hydrate contained nitrates.

Mr. Ross asked whether such sodium hydrate should be used.

The president said that it would probably have to be used.

Mr. Horton said that in one of the German universities the described method of using zinc with the sodium hydrate was almost universal, and was found very satisfactory.

Mr. Farrington said that the same plan worked very well with him.

Mr. Ross said that he would like to see it inserted in the report of Mr. Voorhees along with the granulated zinc or pumice stone.

The president said that it might be recommended to be tested with the samples sent out; it would have to be put in the form of an amendment.

Mr. Voorhees said that he would accept the suggestion as a suggestion merely, not as a recommendation to modify the method, because many chemists did not use zinc at all; the method only directed the

use of granulated zinc "when found necessary to keep the contents of the flask from bumping." In his own laboratory the zinc was not found necessary. He thought the suggestion a very good one in cases where something had to be used to prevent bumping.

The president said that the suggestion would be inserted if there was no objection.

Mr. Lupton moved that the proposed methods for the determination of nitrogen, as amended, be adopted. Carried.

Mr. Frear presented the report of the committee appointed to wait upon the Secretary and Assistant Secretary of Agriculture; the committee had invited them to attend the meeting of the association.

The president stated that the report of Mr. E. H. Jenkins on dairy products was now in order.

Mr. Voorhees said that before proceeding to that report he would like to ask one or two questions in regard to the nitrogen work. Only three of the chemists who analyzed the official samples this year had reported results obtained by their special methods in preparing the acids, and he would be glad to have the experience of the members in regard to the tetra-oxalate, and to know what were the results as compared with the other methods of testing the acid; it seemed to him that this was one of the most important things to be considered in the determination of nitrogen.

Mr. Cooke said that he had been in the habit of resting his faith upon Iceland spar for standardizing the acid until he received the tetra-oxalate sent out by Mr. Caldwell, with which he had made quite a number of determinations. He had been very much pleased with the results obtained on a comparison of the two, their agreement in most cases being within .1 of 1 per cent on the total amount of acid present, that is, .001 of the total acid; in other words, 100 cubic centimeters of one would not take more than 100.1 cubic centimeters of the other, using phenol-phthalein as an indicator.

The president asked Mr. Cooke whether he tried the silver chloride.

Mr. Cooke said that he never succeeded with silver chloride except when he took the precaution, in his case rather difficult, of doing the work late at night, when there was no daylight whatever; in recent work he had not attempted it. The particular sample of tetra-oxalate prepared by Mr. Caldwell had given remarkably close results as compared with Iceland spar and with oxalic acid; the reaction was very sharp.

Mr. Caldwell said that it was necessary to use carefully prepared litmus.

Mr. Cooke said that in the work referred to he believed he had used di-methyl aniline orange for the indicator when testing the Iceland spar, as was his custom; he preferred that to any other indicator; it was not acted on at all by carbonic acid; he would recommend it to the members of the association, and was sure they would like it. With vegetable acids, however, it was good for nothing.

Mr. Frear said that he had bought the so-called pure tetra oxalate and found it worthless; he had therefore made a little for himself prior to receiving that sent out by Mr. Caldwell, and got satisfactory material after a number of crystallizations. That which he had bought was very nearly pure acid oxalate.

Mr. Caldwell said that Baker & Adamson's had been found very good. He would say that cochineal would not answer as an indicator; he had used a carefully prepared litmus. He had never used the indicator suggested by Mr. Cooke, and asked whether that was the ordinary methyl orange.

Mr. Cooke said that it was not; it was an entirely different thing.

By request of the president Mr. Caldwell (vice-president) took the chair.

Mr. Scovell said that he had made quite a number of experiments in regard to standard acid, and had brought a sample, hoping that some other member would do the same and that it might be examined here. After many carefully made experiments he was inclined to believe that the tetra-oxalate gave better results than the silver chloride; with the samples received from Mr. Caldwell his results had been very good, and he had then made a pound or two for his own use, and with that he secured concordant results every time.

Mr. Parsons said that his experience was similar to that of Mr. Scovell; he used tetra-oxalate and invariably got results somewhat (not much) higher than were given by the silver chloride.

The chairman said that the method of standardizing acid was very important; if some definite motion were made the matter could be more readily discussed.

Mr. Voorhees said that the recommendations made by himself, as reporter on nitrogen, and which had been adopted, included the recommendation contained in last year's method in regard to the tetra-oxalate. The object last year, and his object now, was to get an idea as to the use of tetra-oxalate. The recommendation being already in, he would not like to make a motion to take it out. He did not know what motion to make.

Mr. Woods said that with him sodium carbonate invariably gave too low results. He now used sulphuric acid, and by precipitation with barium chloride and by using ammonium chloride of known purity he obtained results that were almost identical. While the results with sodium carbonate had been too low the other (tetra-oxalate) had been too high; the averages of the two had just about hit the mean of the other methods.

The chairman said that if no motion to change were made it would be understood that tetroxalate was to be taken as the standard.

Mr. Cooke inquired whether cochineal was the only official indicator.

The chairman said that he so understood; he thought there should be a modification.

Mr. Cooke said that he would be willing to move that di-methyl aniline orange be inserted as an alternate, but supposed that such a motion would hardly be in order, so few members of the association having used that indicator; he had used it two years, and liked it very well. It might be put in as a suggestion and tried during the year.

The chairman said that, in his opinion, something should be substituted for the cochineal, which was certainly misleading, being exactly the indicator that could not be used. Litmus or di-methyl aniline orange might be substituted.

Mr. Woods said that he had prepared litmus as carefully as he knew how, and had rejected it five years ago as not being at all applicable in the soda-lime or Kjeldahl methods.

Mr. Farrington asked whether the indicator in question was to be used in the analysis or simply for standardizing the acid.

The chairman said that, as he understood, it was to be used in standardizing the reagents. Although it was rather out of order to move a change in methods already passed upon, it was surely desirable to have methods which were right.

It was moved that the methods for the determination of nitrogen be reconsidered. Carried.

Mr. Cooke said that on page 218 of last year's proceedings, under the heading "Apparatus and Reagents" in the Kjeldahl method, the direction to standardize said nothing about the indicator to be used, but from the fact that cochineal was the only indicator mentioned on the following page it would naturally be supposed that cochineal was intended to be used in standardizing. He moved that the words *cochineal or di-methyl aniline orange to be used as an indicator* be added at the end of section 1, page 218, under the heading "Apparatus and Reagents." The motion was seconded.

Mr. Woods asked what would be the use of including cochineal if it could not be used with the tetra-oxalate.

Mr. Myers said that he had understood Mr. Woods to state that litmus could not be used. The association could hardly get along without an indicator, but at present it seemed to be standing between the devil and the deep sea.

Mr. Horton said that perhaps coralline could be used; that was an excellent indicator.

A member stated that he had tried coralline and found that it would not work; he thought it was affected by the organic acid.

Mr. Robinson said that in his experience with the use of di-methyl aniline orange during the past year he found it gave a much sharper reaction than any other reagent which he had used.

Mr. Cooke's motion was carried.

Mr. Huston said that he understood this to refer solely to the standardizing of the acid, and thought that something should be added which would indicate to the workers that they were not to use one in-

dicator in the standardizing and another in doing the work; there was a vast difference between indicators. He moved that section 1, page 218, under the heading "Apparatus and Reagents," be further extended by adding the words *the same indicator to be used in the work as is used in standardizing the acid.*

Mr. Cooke said that such addition seemed to him unnecessary. In the use of indicators in his own work he had found that phenol-phthalein, for instance, would give a certain standard when tetra-oxalate was compared, and that then by comparing the acid made up in that way with ammonia or with caustic soda he got the same results by the use of cochineal. If one had a correct standard the indicator ought to give correct results where it was applicable to the process. For example, di-methyl aniline orange gave correct results in comparing an inorganic acid with an inorganic alkali, but taking the same indicator and using it with an organic acid, the results would not be correct. He thought it would be proper to use one indicator for standardizing and another for using the standard acid where the original indicator was inapplicable.

Mr. Scovell said that he agreed exactly with Mr. Cooke in that regard.

The motion was seconded and carried.

Mr. Woods said that the nitrogen reporter might be instructed to suggest to the stations the trial of different indicators in testing acids, the results to be reported, so that next year the association should have more definite information in respect to indicators than it had now.

Mr. Wiley said that it would take about half an hour to read the report of Mr. Jenkins on dairy products. It was now so near the hour fixed for recess that perhaps the association had better suspend business until after lunch, the afternoon session being set for 2 o'clock.

At 12.15 p. m., on motion, a recess was taken.

AFTERNOON SESSION, THURSDAY.

The convention was called to order by the president at 2 p. m.

Mr. Myers said that the recommendations made by the president in his address were based upon careful consideration as to what would be best for the interests of the association, and it was proper that they should receive due attention. He therefore moved that a committee of three be appointed to consider and report upon the recommendations contained in the president's address. Carried.

The president said that he would appoint the committee soon.

Mr. Caldwell said that he would like to have the report on nitrogen taken up again, as he wished to make a motion, which he thought all would agree to, namely, that sodium carbonate be omitted from the substances by which the standardization might be made. Something had been said against it, nothing had been said in its favor, and it

seemed to him that it would be better to leave it out altogether, even if the matter should have to be taken up again and again. He moved that sodium carbonate, as one of the substances used for the standardization of the acid, be stricken out.

The president said that if no objections were made the subject would be considered as before the convention; if objection were interposed it would be necessary to move a reconsideration.

No objection being made, the motion was held to be in order.

Mr. Myers said that a great many chemists had adopted the sodium carbonate upon the recommendation of Fresenius, and it might be well to understand why it should now be stricken out.

Mr. Caldwell said that it had been spoken of in this convention as inaccurate; he had never tried it, but those who had said that it did not give correct results. He thought that the difficulty of getting the substance pure would be generally admitted. There was every reason to suppose that accurate results could be had with the silver nitrate. If the sodium carbonate were left in some might use it. His objection was based upon what others had said concerning their experience.

Mr. Cooke said that Mr. Caldwell's statement might be made still stronger. Probably there were more laboratories in the United States that used sodium carbonate as a method of standardizing than there were that used all the other methods put together, yet it was very hard to get correct results, and a large share of those obtained were slightly out of the way, though perhaps near enough for commercial work. In his own experience, and that of at least half a dozen chemists who had worked under him, it had been impossible to get an absolutely correct standardization with the purest sodium carbonate they had been able to obtain on the market.

Mr. Huston said that, according to his recollection, his assistant, Mr. Goss, made a precipitation on hydrochloric acid and also by carbonate of soda, and among all his results there was not a readable difference in the burette; he had said, if the speaker's recollection was correct, that of all the methods he preferred the sodium carbonate Mr. Goss had spent a good deal of time on the work, did it carefully, and saw no objection to the use of sodium carbonate, and preferred it as more convenient. It might have been that theirs was an unusually good sample.

Mr. McDonnell inquired how Mr. Caldwell dried his potassium tetraoxalate.

Mr. Caldwell said that it was dried by simple exposure to the air.

The president said it was well known that sodium carbonate had been put in as one of the methods in order that the average of all might be obtained. In his experience last year it was found that sodium carbonate gave the lowest results of all, so that the average would not be as good with that method in as it would if it were out. He had tried the sodium carbonate anywhere obtainable and had made over a hundred experiments, but could not get concordant results. Personally he

thought it very objectionable, as a great many would use it or did use it, sometimes without testing it beforehand.

The motion was seconded and carried.

Mr. Wiley read a communication from Mr. E. H. Jenkins, reporter on dairy products, dated August 23, 1890, stating his inability, through illness, to attend the convention, inclosing his report, and requesting that the same be presented to the association by Mr. Wiley, as secretary.

Mr. Wiley read the report of Mr. Jenkins, as follows:

ABSTRACT OF CHEMICAL LITERATURE RELATING TO THE ANALYSIS OF DAIRY PRODUCTS.

BUTTER.

Mac Farlane (Bull. No. 16, Lab'y of Inland Rev., Dept. of Can.) gives in detail one hundred and fifty analyses of Canadian butter collected from the markets. To thirty-three of the samples exception was taken on account of rancidity, or deficiency of butter fat. Water varied from 3.84 to 19.70 per cent, the average being 8.97; salt varied from 1 to 15.16 per cent, the average being 5.15. No margarin was found in any of the samples, the volatile fatty acids being equivalent, on the average, to 14.9 cubic centimeters $\frac{N}{10}$ potash solution.

Vieth (Milch Zeitg., 1890, 381) gives results of one hundred and ninety-eight butter analyses made during the last six years from samples having the following origin: Schleswig-Holstein, Denmark, Sweden, France (salted and unsalted), and England. The summary of these analyses is as follows:

Fat varied from 80 to 90 per cent. In three cases it fell below 80; in one it was over 90 per cent.

Water varied between the extremes 8.03 and 17.25; in most cases it was between 11 and 15 per cent. While a high per cent of water in butter is undesirable, too low a per cent is likewise detrimental, not only because it can only be caused by excessive working of the butter, but also because there is danger that the salt used in salting will either be imperfectly dissolved, or, once dissolved, will crystallize out if water evaporates slightly from the butter.

Salt, in Schleswig-Holstein butter, never rose above 2 per cent, and in several cases was less than 1 per cent. In Danish, Swedish, and French butters it was between 1 and 3 per cent.

In unsalted French butter there was generally found 0.1 per cent or less of chlorine. Where 0.2 or over were found the author judges that the butter has been washed in brine.

Especially valuable, as a basis of judging of the method of making the butter, is the relation between water and the sum of the other ingredients exclusive of fat and salt. In milk "serum," *i. e.* a fat-free milk to 100 parts of water, there are 10 parts of dry matter. About the same relation must exist in buttermilk free from fat, *provided* that radical changes have not taken place in the substance of the milk. When sweet or only slightly sour cream or milk is buttered the relation of water to solids not fat and salt will be about 100 to 10. But if the milk or cream were decidedly sour and in consequence casein had coagulated in larger and firmer lumps, the ratio of solids not fat or salt to water would be considerably greater than 10 to 100, while if the butter were washed the ratio would be considerably less than 10 to 100. The author regards a ratio of 9 or 10 to 100 as indicating nothing more than rinsing the butter with water but a lower ratio still as indicating washing.

St. Bondzynski and H. Rufi (Landwirthschaftl. Jahrb. d Schweiz, 1889, Chem. Zeitg.

Repert. 1890, 20) propose two methods of determining volatile fatty acid in butter simpler than Wollny's.

(1) Four to 5 grams of butter are quickly saponified with 50 to 60 cubic centimeters of alcoholic $\frac{N}{2}$ potash solution, the excess of alkali is exactly neutralized with $\frac{N}{2}$ hydrochloric acid, the alcohol is expelled by evaporation, the soap is decomposed by hydrochloric acid and the separated insoluble fatty acids are filtered and washed with hot water, dissolved in alcohol and titrated with $\frac{N}{2}$ or $\frac{N}{4}$ potash solution. The difference between the quantity of potassium hydrate combined with all the acids and that required to neutralize the non-volatile (insoluble) acids represents the alkali necessary to neutralize the volatile acids.

(2) The butter fat is saponified as before, the alcohol expelled by evaporation and the aqueous soap solution in an Erlenmeyer flask is decomposed with a quantity of $\frac{N}{2}$ sulphuric acid exactly equivalent to the alkali used for saponification.

The flask is fitted with an inverted condenser, and the contents, made up to 400 or 500 cubic centimeters, are heated till the aqueous solution under the melted fat has become perfectly clear. Then the separated insoluble acids are washed out, and in the filtrate the volatile (soluble) acids are titrated with $\frac{N}{2}$ alkali solution.

Both methods give results which agree with each other and with the results of distillation. The quantity of volatile fatty acids and of their glycerides may be expressed in per cent of the butter fat. To this end the insoluble acids are rinsed into a tared flask with ether, and after evaporation the residue is dried and weighed, and then titrated. The alkali required corresponds to its equivalent of glycerol from which the glycerides of the insoluble acids are reckoned. This subtracted from the total quantity of the fat gives the quantity of glycerides of volatile acids.

The authors also state that free volatile acids can only be detected in butter which is in an advanced state of decomposition. Fresh butter contains free insoluble acids in small quantity, and rancidity is to be ascribed to the increase of these free, *insoluble* acids.

E. H. Amagat and F. Jean (Compt. rend. 1889, 109, 616, Abstr. Chem. Zeitg Repert., 1889, 308) describe the use of their oleorefractometer, by which the presence of oleomargarine in butter is easily detected. The butter is melted at a low temperature, filtered through muslin, and dissolved in ether. This solution is washed with warm water, filtered, and after evaporation of the ether, is dried at 110°. The fat of genuine butter, so prepared, gives a constant deviation of 35° to the *left* compared with the fat of ox hoof oil as the standard. Margarin prepared from kidney fat of neat stock shows 19°, and margarin prepared by the Niege-Mouries process, 15°. Butter with 50 per cent of this margarin shows 23°; with 25 per cent, 28°, and with 10 per cent, 32°. An addition of less than 10 per cent is readily detected. The vegetable oils give a deviation to the *right*.

C. Viollette (Compt. rend. 1890, 111, 348) indorses the oleorefractometer as a useful instrument in distinguishing between pure butter and margarin. Pure butter varies between — 33° and — 27° in the deviation produced, margarin between — 15° and — 8°.

G. Ambühl (Chem. Zeitg. 12, 392, Abstr. Zschr. analyt. Chem. 1889, 18, 369) uses an apparatus to determine the apparent specific gravity of butter fat at 100° C., which is essentially like Soxhlet's apparatus for determining the specific gravity of the etherial fat solution obtained from milk. Soxhlet's water jacket is simply used as a steam jacket to keep the temperature at 100°.

Ed. von Raumer (Arch. f. Hyg. 1888, 8, 407 Abst. in Chem. Zeitg. Repert., 1889, 41) considers the Meissel-Reichert method of determining the volatile fatty acids of butter to be the most reliable. He prefers to saponify the fats in an open dish, con

stantly stirring with a pestle to expel alcohol as quickly as possible and to avoid long heating, which even at 95° C. decomposes fatty acids. He claims, in opposition to Wollny, that the presence of carbonic acid exerts little influence on the result. The endeavor to obtain the total quantity of volatile fatty acids by repeated distillation he claims is useless, for there is constant decomposition going on, with formation of volatile acid.

P. van Hamel-Roos (Rev. internat. des falsifications 1890, 3, 116; Abstr. Chem. Zeitg. Repert., 1890, 87) in three samples of butter found 0.8, 11.2 and 12.4 cubic centimeters $\frac{N}{10}$ alkali (by Reichert's method, 2.5 grams) respectively. He was informed that the first was margarin, the second butter with 25 per cent cocoa butter, and the third genuine butter. Cocoa butter alone required 4.5 cubic centimeters $\frac{N}{10}$ alkali.

P. Cosbetta (Chem. Zeitg. 1890, 406) from careful experiment concludes—

(1) The content of volatile fatty acids in butter (determined by Wollny's modification of Reichert-Meissel) suffers a decided progressive loss in becoming rancid.

(2) This loss is not very considerable; the maximum in his experiments was 2 cubic centimeters $\frac{N}{10}$ alkali.

(3) No volatile fatty acid is withd rawn from rancid butter by washing with water or sodium bicarbonate.

L. F. Nelson (Zeitschr. analyt. Chem. 1889, 28, 175; Abstr. in Chem. Zeitg. Repert. 1889, 121) finds that the volatile acids from the conventional quantity of collostrum fat require only 18.5 to 20 cubic centimeters of alkali for neutralization, instead of 25 cubic centimeters or more. In the course of five to seven days after calving the maximum content of fatty acids is reached, and after a few days slowly and regularly decreases till it equals only 24 cubic centimeters of alkali at the end of lactation. Season of the year and feeding have no effect on the quantity of volatile fatty acid.

P. Vieth (Analyst 15, 45) presents in some detail the results of 20,674 analyses of milk, 1,123 analyses of cream, and 104 samples of butter; the latter of English, French, Danish, Swedish, and German origin. In certain samples of butter from Kiel the volatile fatty acids determined by Wollny's method were equivalent to only 21.1 cubic centimeters $\frac{N}{10}$ alkali, but that they were pure butter was not demonstrated.

MILK.

Hittcher (Mitth. a. d. Versuchs-Molkerei Kleinhof-Tapian, abstr. in Vierteljahresschr. d. Chem. d. Nahrungs- u. Genussmittel, 1890, 5, 2) has made a special study of the quality of milk of individual cows. Among the most important observations are these:

(1) Certain cows in the whole period of lactation produced twice as much milk fat as others.

(2) During heat, the per cent of fat in the milk of certain cows sank extraordinarily: as low as 0.7 per cent, while others were scarcely affected at all.

(3) Poor quality of milk is a trait which is transmitted from a cow to her offspring.

(4) Quality of milk is an individual peculiarity and high quality of milk is perhaps sooner and cheaper obtained by selection of cows than by rich feeding.

M. Kühn (Milch-Zeitg., 1889, 47, 923) has made analyses of milk from eleven individual cows new in milk and from eleven others towards the end of lactation, both sets being of approximately the same age, of the same strain, and having the same food and care. He finds that on the average the cows new in milk gave considerably more milk than the others, but less rich in solids, fat, and albuminoids; sugar and ash were about the same. In a single case the specific gravity of the milk of a single cow was 1.0272 and in three cases among the cows old in milk and three in new milk cows the specific gravity was below 1.029, which is regarded as the lowest limit for pure milk.

The milk of old milkers showed the greater variations in dry substance, sugar, and especially in fat.

By the use of Fleischmann's formulas, according to the tables in Milchwirthchaftl. Taschenbuch 1889, for calculating solids or fat, in all cases the dry matter runs from 0.1 to 0.6 per cent higher than was found by analysis, and the fat correspondly lower. The author suggests that the formulas may not hold perfectly for all races of calves or for all kinds of feed.

F. J. Lloyd (Jour. Chem. Soc., 1890, 57, 201) gives analyses of abnormal milk from two cows in a herd. The cows were to all appearance healthy. Their food was ample, and other cows of the same herd and under the same conditions were giving rich normal milk. They were cross bred Shorthorns and one of the two appeared to have some Dutch blood. The quantity of milk was "not large, and is decreasing rapidly." It was about 38 pounds per day in November, and fell in one case to 8 and in the other to 18 pounds in January. Some of the samples were drawn by the author himself after seeing the cows milked. Others were sent by the owner after supervising the milking.

In the morning milk, which was the poorest, the total solids ranged from 10.04 to 11.88; the fat from 2.17 to 3.44; solids not fat from 7.50 to 8.47.

Isbert and Venator (Ztschr. f. angew. Chem., 1890, 85; abstr; Chem. Zeitg. Repert., 1890, 41) find the mixed milk of fifty cows from one stable to have the following composition:

Specific gravity at 15°		1.0355
Fat	per cent..	2.6
Solids	do...	10.9
Creamometer	do...	7.0

Perron (Jour. Phar. Chim., 1890, 5 ser. 21, 63; abstr. Chem. Zeitg. Repert., 1890, 42) notes an adulteration of milk with olive oil emulsified with borax or yolk of egg. The fat separates from such adulterations rather incompletely. Borax is readily detected by the spectroscope in the milk ash, and oil by determining the freezing point of the fatty acids, which in acids from pure butter fat lies between 37.5° and 38.5°, while the acids from oils melt at a temperature lower by some 10°.

H. D. Richmond (Analyst, 1889, 14, 2), after trying the preservative action of alcohol, carbon disulphide, ether, dichlorophenol, chloroform, and terpenes, which were unsatisfactory, found that milk could be most satisfactorily preserved by the addition of 0.5 per cent of commercial hydrofluoric acid. This is equivalent to one drop in 10 cubic centimeters. The casein was precipitated, but by gentle shaking is brought into such a fine state that sampling is easy and the fat is evenly and thoroughly distributed. The milk must be *fresh* when treated. The author gives results showing that the determinations of solids and fat made in the fresh samples and in the same samples after being kept for periods varying from a month to nearly a year, were nearly identical.

Schweissinger (Phar. Ctrlb., 1890, 6; abstr. in Vierteljahresschr. Nahrungs-u. Genussmittel, 1890, 5, 16) describes an areopycnometer designed to determine the specific gravity of milk when only a small quantity of milk is available. (See Milch Zeitg., 1890, 4.)

H. D. Richmond (Analyst 1890, 16, 170) emphasizes the fact that the specific gravity of milk must not be determined until twenty-two hours after milking, as in the mean time it becomes denser, and after shaking the milk in preparation for the specific gravity determination special care must be taken to remove bubbles which are held by milk tenaciously. Referring to his formula for calculating fat from the solids and density, $T = 1.17\ F + \frac{263\ G}{D}$ he now extends the formula to include the calculation of milk sugar and proteids; the density, fat, total solids, and ash being known. P = proteids; T = total solids; A = ash; F = fat; D = density; water at 60° Fah. being taken as 1; and G = 1000 D − 1000.

The formula is $P = 2.8\ T + 2.5\ A - 3.33\ F - .7\frac{G}{D}$

The difference between total solids and the sum of fat, proteids, and ash gives milk sugar. The assumption that the solids contain no other substance involves a small error. A second and larger error is due to the fact that the ash of milk does not represent the salts of milk because of the destruction of organic salts by ignition. By use of the formula the author calculates the influence of 1 gram of each constituent in 100 cubic centimeters on the density, and from that the density in solution, and compares this calculated density with direct determinations of the density of the constituents made by different observers, as follows:

	Influence of 1 gram in 100 cubic centimeters	Calculated density.	Observed density.	Observer.
Fat	0.76	0.929	0.93	(Fleischmann, Jour. f. Landw., xxxiii, 251.)
Sugar	4.00	1.667	1.65	(Many observers.)
Proteids	2.57	1.346	1.34	(Dupré, Analyst, viii, 248.)
Ash	7.57	4.12	3.00	(Dupré, *loc. cit.*)

The cause of disagreement in ash has been pointed out.

G. Mariani (Italian Experiment Stations, xxii, 1889; Abstr. in Chem. Zeitg., 1890, 64), for the absorption of milk in the determination of solids and fat, indorses the use of paper pulp extracted thoroughly with petroleum ether, which has been recommended by Gaunter. He found that the method of drying the milk by itself without any absorbent, and drying it with wood paper pulp gave nearly identical results. In twelve determinations made by each method the greatest difference between the total solids found by the two methods was less than 0.1 per cent. Drying with sand gave somewhat higher results. The drying with pulp was quicker done than with sand. When 10 to 12 grams of milk were used with 5 grams of pulp, the drying was finished in three hours. The author considers the sand method preferable where great accuracy is required.

The fat determinations, made by extracting the dried sand or pulp residues in a Soxhlet's extractor, with absolute ether, showed satisfactory agreement. The greatest difference, among twelve determinations, was 0.215 per cent, and the average difference 0.09 per cent. He found five hours sufficient for the complete extraction of fat from sand, while the extraction of paper pulp was complete in three hours.

P. Vieth (Analyst, 15, 45) finds a close relation between the per cent of non-fatty solids, and ash in milk and cream. The ash is equal to just 8 per cent of the non-fatty solids. He regards this as a useful check in analysis and a test of the normal quality of a milk.

P. Radulescu (Mittheil. a. d. phar. Inst. u. Labor. f. angew. Chem. d. Universität Erlangen, v. A. Hilger, 1890, 3, *93; Abstr. Chem. Zeitg. Repert., 1890, 174) has examined the statements regarding the determination of the specific gravity of milk serum as a means of judging of its genuineness.

To coagulate milk, 100 cubic centimeters of milk are heated with 2 cubic centimeters of 20 per cent acetic acid on a waterbath, so that the milk itself is kept at a temperature of 55° to 65° for five minutes. It is not stirred during the time. The clear serum is then filtered off and its specific gravity determined by the pycnometer or the Westphal balance.

The author concludes—

(1) The specific gravity of a serum or whey of normal milk is never less than 1.027.

(2) Addition of 10 per cent of water to normal milk lowers the specific gravity of the serum by 0.0005 to 0.001.

(3) The dry matter and fat of serum should always be determined.

(4) The serum always has 6.30 to 7.5 per cent of solids and 0.22 to 0.28 per cent of fat.

(5) Addition of 10 per cent of water to normal milk causes a diminution of solids in the serum of 0.3 to 0.5 per cent.

Charles Rice (Jour. Analyt. Chem., 1890, 4, 155) proposes to substitute for Adams's paper coils for fat determinations in milk "absorbent gauze," also called "bleached hospital gauze," a light open-mesh cotton fabric, having about forty threads to the linear inch, and weighing about 1¾ ounces per square yard.

"The milk coils, or cartridges, consist of a small roll of this gauze, inclosed in a wrapper of blotting paper, and their mode of preparation is as follows:

"Spread out a square yard of the gauze on a flat surface; fold it twice in one direction to reduce it to 36 by 9 inches; then fold it upon the long side in laps of 1¾ inches in width, so that when the whole is folded it will present a strip of 1 yard in length, and about 1¾ to 1⅞ inches in width, and will consist of some eighteen to twenty layers.

"Now begin to roll the strip up on the narrow end, like a bandage, but not too tight, until about 5 or 5½ inches of the gauze have been rolled up; cut the strip slantingly, that is, not perpendicular to its body, but under an angle, so as not to cause "bunching" when wrapped in paper. Place the roll upon a strip of blotting paper 4 inches long and 2¾ inches wide, and roll the latter over it so as to have it (the paper) project at one end about one-fourth inch over the gauze coil, and about three-fourths inch at the other; then tie the coil with two threads. It will thus be 2¾ inches long and about seven-eighths inch in diameter." Here is given a figure of the coil with explanations.

"The larger compartment of this cartridge serves as a funnel, into which the full quantity of the milk to be tested is poured at once. A coil of this kind, intended for the smallest size of Soxhlet's extractor, will easily take from 8 to 10 grams of milk, and the latter will never entirely soak down to the bottom of the paper wrapper. If it should soak to the bottom of the gauze coil, this will do no harm, as it is one-fourth inch above the end of the paper."

Babcock (Wis. Exp. Sta. Bull., No. 24) describes a new method for determining fat in milk, especially adapted to creameries and cheese factories, as follows:

DESCRIPTION OF APPARATUS AND CHEMICALS REQUIRED.

(1) *Test bottles* (Fig. 1.)—These are of the same form as the bottles used in Short's test, but are made a little smaller and of heavier glass. They should contain up to the neck not less than 40 cubic centimeters nor more than 45 cubic centimeters. Each division of the graduated scale upon the neck represents 0.04 cubic centimeters, and in order to facilitate the reading the neck is made of such a diameter that the marks of the scale are about 1½ millimeters apart. Five of these divisions are equivalent to 1 per cent of fat when 18 grams of milk are used in the test, it being assumed that the specific gravity of the butter fat, at the temperature at which the reading is made (about 120° F.), is 0.9.

(2) *Pipette for measuring milk.*—This may be of any form, but that shown in Fig. 2, with a rather wide opening at the lower end to allow the milk to run out rapidly, is to be preferred. It should contain, when filled to the mark, 17.6 cubic centimeters. A pipette of this size will deliver a little less than 17.5 cubic centimeters of milk. The quantity of milk required for the test sample of 18 grams is 17.44 cubic centimeters, if the milk has the average specific gravity of 1.032.

(3) *A measure for the acid.*—A graduate or cylinder of glass (Fig. 3), with a lip to pour from and a single mark at 17.5 cubic centimeters, is the best form for general use. In laboratories a large burette, holding 100 or 200 cubic centimeters with marks at each 17.5 cubic centimeters and having a glass stopcock, may be used to advantage, but on account of the liability of breakage is not to be recommended in factories or private dairies.

(4) *A centrifugal machine.*—Figs. 4 and 5 show the construction of the machine used by us. The gear in this apparatus is so proportioned that the wheel which

carries the test bottles makes about ten revolutions to one of the crank ; with this it is easy to impart from seven to eight hundred revolutions per minute to the horizontal wheel. Any arrangement that will do this, either by belt or gear, will answer the purpose. Within the horizontal wheel (*a*, Fig. 5) are placed sectors (*b*) made from heavy sheet copper to which are soldered cups or tubes (*c*), inclined so as to make an angle of about 30° with the horizontal, for the support of the test bottles. The horizontal wheel is surrounded by a copper jacket (*d*, Fig. 5) with a cover. This serves the double purpose of supplying heat for the test by pouring hot water into it, or by heating water directly with a lamp placed beneath, and of arresting the hot acid which would fly off if a bottle should break.

(5) *A kerosene or gas lamp* for heating two or three quarts of water to boiling.

(6) *Commercial sulphuric acid*, having a specific gravity of 1.82 or about 90 per cent pure. If only the pure acid is available, it should be diluted with water to the strength indicated.

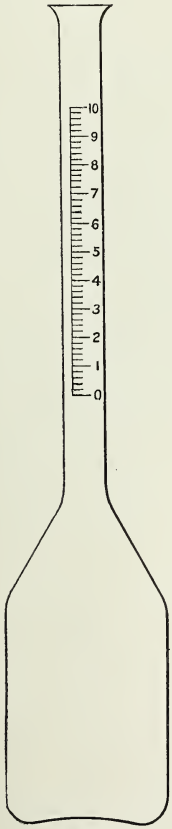


Fig.1.

Fig.2.

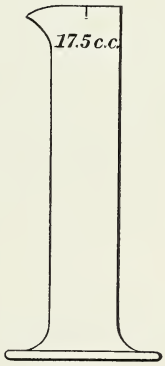


Fig.3.

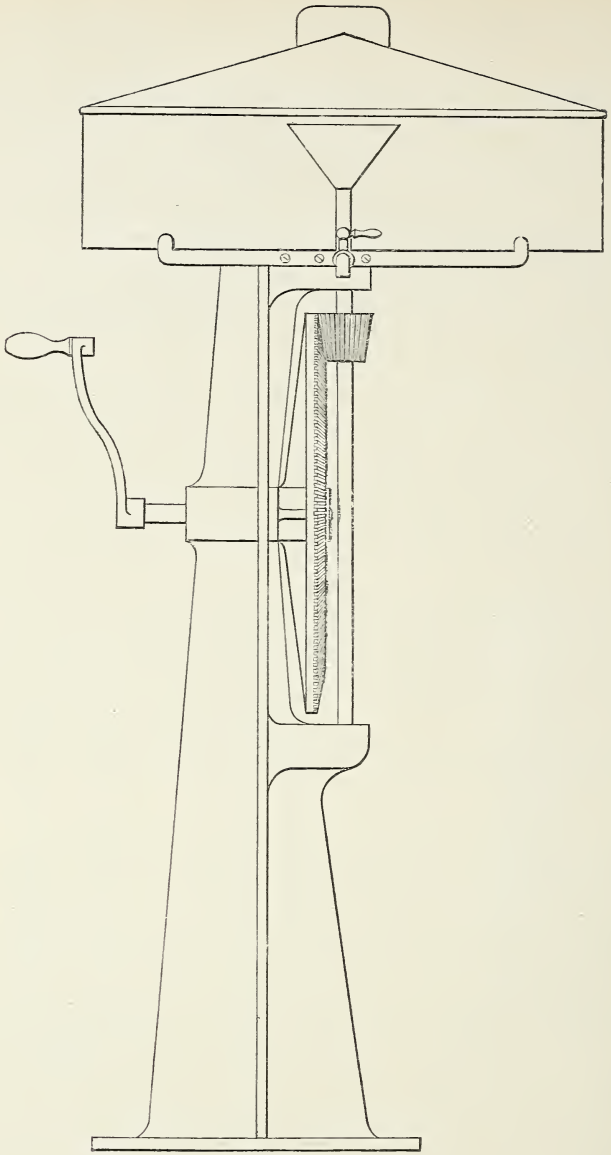


Fig. 4.

THE TEST.

Sampling the milk.—Every precaution should be taken to have the sample represent as nearly as possible the whole lot of milk from which it is taken. Milk fresh from the cow, while still warm and before the cream has separated in a layer, may be thoroughly mixed by pouring three or four times from one vessel to another. Samples taken at once from milk mixed in this way are the most satisfactory of any. Milk that has stood until a layer of cream has formed should be poured more times until the cream is thoroughly broken up and the whole appears homogeneous. No clots of

cream should appear upon the surface when the milk is left quiet for a moment. With proper care any milk that has not coagulated, or that has not been exposed to the air until the surface of the cream has become dried, may be mixed so that a representative sample may be taken. Milk should not be poured more times than is necessary, as continual mixing in this way is liable to churn the cream, forming little granules of butter that quickly rise to the surface. When this occurs it is impossible to obtain a fair sample. Milk is sometimes churned by being transported long distances in vessels that are not full. When this occurs it is useless to make an examination.

It is impracticable to sample a large amount of sour milk, but a small sample of a pint to a quart may be thoroughly mixed by adding five per cent of strong ammonia water which will dissolve the curd and permit a uniform mixture being made. When ammonia is added, the final results should be increased by 5 per cent. Samples from sour milk are, however, never as satisfactory as those taken when the milk is in a proper condition.

Measuring the milk.—When the milk has been sufficiently mixed, the milk pipette is filled by placing its lower end in the milk and sucking at the upper end until the milk rises above the mark on the stem; then remove the pipette from the mouth and quickly close the tube at the upper end by firmly pressing the end of the index finger upon it to prevent access of air; so long as this is done the milk can not flow from the pipette. Holding the pipette in a perpendicular position, with the mark on a level with the eye, carefully relieve the pressure on the finger so as to admit air slowly to the space above the milk. When the upper surface of the milk coincides with the mark upon the stem, the pressure should be renewed to stop the flow of milk. Next, place the point of the pipette in the mouth of one of the test bottles, held in a slightly inclined position so that the milk will flow down the side of the tube leaving a space for the air to escape without clogging the neck, and remove the finger allowing the milk to flow into the bottle. After waiting a short time for the pipette to drain, blow into the upper end to expel the milk held by capillary attraction in the point. If the pipette is not dry when used it should be filled with the milk to be tested, and this thrown away before taking the test sample. If several samples of the same milk are taken for comparison, the milk should be poured once from one vessel to another after each sample is measured. Neglect of this precaution may make a perceptible difference in the results, through the separation of cream, especially when the milk examined is rich.

Persons who have had no experience in the use of a pipette will do well to practice a short time by measuring water into a test bottle before attempting to make an analysis. The manipulation is easily acquired, and with a little practice milk may be measured nearly as rapidly with a pipette as with a graduate, and with much greater accuracy.

Adding the acid.—When the milk has been measured into the test bottles the necessary amount of sulphuric acid may be added immediately, or the bottles may be left for a day or two without materially changing the results; samples that have remained in the test bottles more than a week have given the same amount of fat as samples tested immediately after being measured. If the milk has become coagulated the curd should be broken up by shaking the test bottle before the acid is added.

The volume of commercial sulphuric acid required for a test is approximately the same as that of the milk, 17.5 cubic centimeters for the ordinary test. If too little acid is added, the casein is not all held in solution throughout the test, and an imperfect separation of the fat results. If too much acid is used the fat itself is attacked. The acid need not be measured with great accuracy; any quantity between 17 and 18 cubic centimeters will answer the purpose.

Great care must be taken in handling the acid to avoid getting any of it upon the skin or clothing, as it is very corrosive. If by accident any is spilled upon the hands or clothes, it should be washed off immediately, using plenty of water. A prompt

application of ammonia water to clothing upon which acid is spilled may prevent the destruction of the fabric and restore the color.

When all of the samples of milk to be tested are measured ready for the test, the acid measure is filled to the 17.5 cubic centimeter mark with sulphuric acid, and from this it is carefully poured into a test bottle, containing milk, that is held in a slightly inclined position for reasons given in directions for measuring the milk. The acid being much heavier than milk sinks directly to the bottom of the test bottle without mixing with the milk that floats upon it. The acid and milk should be thoroughly mixed together by gently shaking with a rotary motion. At first there is a precipitation of curd from the milk, but this rapidly dissolves. There is a large amount of heat evolved by the chemical action, and the solution, at first nearly colorless, soon changes to a very dark brown, owing to the charring of the milk sugar and perhaps some other constituents of the milk.

Upon standing a short time the fat begins to collect upon the surface, not in a clear layer, but having at first the appearance of a dirty cream. The separation of fat by gravity alone is not complete, even when the bottles are left standing for several hours; with the centrifuge, however, a perfect separation is accomplished in a few minutes.

Whirling the bottles.—The test bottles containing the mixture of milk and acid may be placed in the machine directly after the acid is added, or they may stand several hours without harm. An even number of bottles should be whirled at the same time, and they should be placed in the wheel in pairs opposite to each other, so that the equilibrium of the apparatus will not be disturbed. When all of the test bottles are placed in the apparatus, the cover is placed upon the copper jacket, and the machine is turned either by hand or by power at such a rate that the wheels carrying the bottles will make from six to eight hundred revolutions per minute, and this motion must be kept up for six or seven minutes. If this wheel is less than about 20 inches in diameter the speed should be greater, or else the whirling should be continued for a longer time.

When the bottles are placed in the machine directly after the acid is added, the separation may be effected without any extra heat, as that caused by the chemical action is sufficient to keep the fat liquid. If the bottles have stood after the acid is added until the contents are cooled below 100° F., the water in the tank should be warmed to about 200° F. before putting the bottles in the machine. The bottles should not be kept heated in the machine as high as the boiling point of water while the separation is being effected. The proper degree of heat may be obtained by lighting the burner or kerosene stove under the jacket when the machine is started, so much water having been poured into the jacket as will be just heated to boiling when the whirling is finished. In this way hot water is always available for filling the tubes at the proper time. In creameries heat can be most easily supplied by steam connection with the boiler. If the machine is stopped after about six minutes a layer of fat will be found upon the upper surface of the liquid in the tubes. This fat will not usually be clear; this, however, will make no difference in the result, as the subsequent treatment will clarify it.

As soon as the bottles have been sufficiently whirled they should be filled to the neck with hot water. This is most conveniently done by placing a vessel containing boiling water above the machine, and by means of a siphon, made from a small rubber tube with a glass tip, running the water directly into the bottles without removing them from the wheel. The flow of water can be perfectly controlled by a pinch-cock upon the rubber tube. If only a few tests are to be made the bottles may be easily filled with a pipette, or by pouring from a graduate. The cover should then be replaced and the machine turned for one or two minutes, after which more hot water is added, filling the tube to about the 7 per cent mark. The fat will slowly rise into the graduated tube, losing its cloudy appearance as it passes through the hot water. When all of the bottles are filled the cover is put upon the tank and the machine

again turned for a short time. During this time the water in the tank should be kept hot, either by placing a lamp or kerosene stove beneath it, or by pouring in a quantity of boiling hot water before starting the machine. If the fat in some of the tubes still has a cloudy appearance, the cover should be placed upon the tank and heat applied for a few minutes, when the fat should become clear and in condition to be measured. The clearing may be hastened by whirling the tubes while hot. When the bottles are allowed to cool off to a point where the fat will crystallize and then warmed again, the fat will usually be much clearer than before, but as this does not materially change the volume of fat it is considered unnecessary. Even a slight cloudy appearance does no harm.

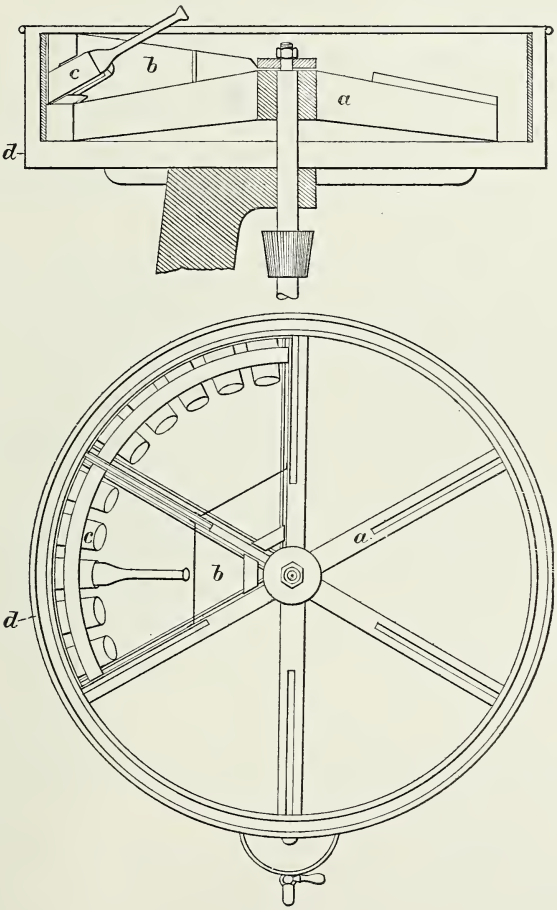


Fig. 5.

Measuring the fat.—The fat when measured should be warm enough to flow readily, so that the line between the acid liquid and the column of fat will quickly assume a horizontal position when the bottle is removed from the machine. Any temperature between 110° and 150° F. will answer, but the higher temperature is to be preferred. The slight difference in the volume of fat due to this difference in temperature is not sufficient to materially affect results. A difference in temperature of 40° F. will make less than one-tenth per cent difference in milk containing 5 per cent of fat. To measure the fat, take a bottle from its socket, and holding it in a perpendicular position

with the scale on a level with the eye, observe the divisions which mark the highest and lowest limits of the fat. The difference between these gives the per cent of fat directly. The reading can easily be taken to half divisions or to one-tenth per cent.

If the column of fat is less than about one division, as will sometimes happen with skim milk, buttermilk, or whey, it may assume a globular form instead of a uniform layer across the tube; when this occurs the fat can usually be estimated with sufficient accuracy by simple inspection, but if an accurate reading is desired it may be obtained by taking four samples of the milk in four test bottles, and after treating them in the usual way, until the bottles are ready to be filled with water, adding water to three of them only, filling them as full as possible without running them over. After whirling them for a minute to bring the fat all into the neck, the fat may be poured off from these three tubes into the fourth. If any fat remains adhering to the sides of these tubes, they should be filled a second time with water and the remaining fat poured into the fourth bottle, which is then filled with water, whirled and the reading taken; this divided by four will give the per cent of fat.

A better way would undoubtedly be to have a special test bottle, holding three or four times as much as the ordinary bottle, that could be used for skim milk, buttermilk, and whey. Three or four times the usual test sample could then be taken, and by adding the proper quantity of acid, the test could be made without transferring the fat.

Cream.—The chief difficulty in testing cream lies in the sampling. Cream that is sour, or that has been exposed to air until the surface has dried, can not be accurately sampled. The same is true of centrifugal cream that is badly frothed. Sweet cream, from Cooley cans, that is not too thick to flow readily from the pipette, may be tested with satisfactory results. The process, however, must be modified slightly from that used with milk, as the amount of fat in cream is so large that it can not be measured in the ordinary test bottle if the usual quantity is taken for the test, besides a much greater error results from the cream which adheres to the pipette than with milk. Both of these difficulties may be overcome by taking two or three test bottles and dividing the test sample into as nearly equal portions as can be judged by the eye. The pipette is then filled with water and this is run into the tubes in the same way as the cream. If three bottles are taken the pipette is filled with water a second time and emptied into the bottles as before. This serves to rinse the cream from the pipette, and at the same time to dilute it to a point where it can be tested in the same way as milk. The bottles are then treated in the usual manner, and the reading of the tubes added together for the per cent of fat in the cream.

Owing to the low specific gravity of cream, the test sample, if of the same volume, will weigh less than that of milk, and consequently the per cent of fat as shown by the scale will be less than is found by gravimetric analysis, in proportion as the weight is less than 18 grams. Where a delicate balance is available, this error may be entirely avoided by weighing the cream used in a test, and calculating the per cent of fat by multiplying the scale reading by $\frac{18}{a}$, a being the weight of cream taken.

If 17.6 cubic centimeters of cream is taken, and the portion adhering to the pipette is rinsed into the test bottle, a close approximation of the true result may be obtained without weighing by correcting the scale reading as follows: For a scale reading of 20 per cent, add 0.25 per cent; for a scale reading of 15 per cent, add 0.1 per cent. Readings between these may be corrected in proportion. Below 10 per cent no correction is necessary.

Accuracy of test.—During the past month a considerable number of comparative analyses have been made by the gravimetric method and by the new test. These are given in the following table, and show the substantial accuracy of the method. The figures are not selected, but represent all of the samples of milk analyzed by both methods between May 27 and July 15. The gravimetric analyses were made by drying the milk upon asbestos and extracting with ether. In analyses by the new test no readings were made to less than one-half a division of the scale, or to 0.1 per cent.

The figures in the second decimal place are derived from corrections for the quantity of milk used in the test, 15 and 20 cubic centimeters of milk having been taken in many of the preliminary trials. These comparative analyses were mostly made with milks from single cows, as such present greater difficulties than mixed milk.

Comparative results by the new and gravimetric methods.

[Per cent of fat.]

Kind of milk.	By new test.	By gravimetric analysis.
Single cow, Bunn; grade, Holstein	3.64	3.72
Skim milk	0.20	0.21
Single cow, Bessie's heifer, $\frac{15}{16}$ Jersey	6.44	6.55
Single cow, Mattie; grade, Holstein	3.63	3.60
Single cow, Topsy; grade, Holstein	3.35	3.33
Cream	22.98	22.69
Single cow, Bunn; grade, Holstein	3.29	2.99
Single cow, Rose; grade, Jersey	3.93	4.00
Single cow, Sylvia's heifer; high grade, Jersey	4.57	4.73
Single cow, Doubtful; high grade, Jersey	4.98	4.91
Cream	21.25	21.47
Single cow	3.75	3.87
Mixed milk	4.69	4.77
Single cow, Flossie; registered Jersey	5.31	5.38
Single cow, Bessie; high grade, Jersey	5.08	5.14
Single cow, Nettie; high grade, Jersey	5.32	5.40
Single cow, Daisy; grade, Jersey	4.69	4.56
Single cow, Rose; grade, Jersey	5.39	5.37
Mixed	5.98	5.94
Single cow, Jersey	6.91	6.87
Whey	0.68	0.61
Cream	17.96	18.08
Skim milk	0.89	0.81
Single cow, Bessie's heifer, $\frac{15}{16}$ Jersey	6.95	6.81
Single cow, Sylvia; grade, Jersey	6.44	6.43
Single cow, Dolly; grade, Jersey	5.75	5.64
Single cow, Bryant; grade, Jersey	4.22	4.24
Single cow, Daisy; grade, Jersey	4.69	4.70
Single cow, Bunn; grade, Holstein	2.87	2.93
Single cow; grade, Jersey	4.10	4.03
Single cow, Daisy's heifer; grade, Jersey	4.22	4.02
Single cow, Galena; high grade, Jersey	4.45	4.31
Single cow, Topsy; grade, Holstein	3.40	3.23
Single cow, Mattie; grade, Holstein	3.28	3.41
Single cow, Annie Johnson; registered Jersey	5.04	5.10
Single cow, Annie Johnson; registered Jersey	5.16	5.22
Buttermilk, sweet cream	3.00	3.09
Cream	16.10	16.13
Buttermilk, sour cream	0.40	0.58
Buttermilk	1.40	1.63

Applications of the method.—The test gives good results not only with milk and cream, but also with the waste products, skim milk, whey and buttermilk, so that those using it can easily watch their work and determine where and what the losses are.

To those who have facilities for weighing, it offers a rapid and quite accurate method for the estimation of fat in condensed milk and in cheese. For the examination of condensed milk about 8 grams may be weighed into a test bottle, then after adding about 10 cubic centimeters of water, the test may be conducted in the same way as with milk, the per cent of fat being obtained by multiplying the reading by $\frac{18}{a}$, *a* being the weight of substance taken for the test.

For the estimation of fat in cheese, about 5 grams should be weighed in a small beaker, and from this transferred, as completely as possible, to a test bottle; the beaker is then rinsed into the test bottle with a mixture of 15 cubic centimeters of water and 18 cubic centimeters of acid. By shaking the bottle for a short time the curd will all be dissolved, leaving the fat free. The test is then made as with milk, the per cent being obtained in the same way as with condensed milk.

Several tests have been made with both condensed milk and with cheese, which have given a clear separation of fat. The only comparisons with the gravimetric method are the following:

Analysis of condensed milk and cheese.

[Per cent of fat.]

	New Method.	Gravimetric.
Cream cheese	57.05	56.80
Condensed milk	9.65	9.47
Cheese	34.87	35.46
Cheese	33.73	33.77

Time required for making the test.—On account of the large number of tests which may be carried along together and the little attention which each demands, the average time required for a test is very small. Two samples of milk may be tested in duplicate in fifteen minutes, including all of the work from the mixing of samples to the cleaning of the bottles. After the milk has been measured, sixty tests may be made in less than two hours, including the cleaning of the bottles.

Expense of the test.—The cost of the test will depend upon the price of commercial sulphuric acid. The wholesale price of this acid is about 2 cents per pound. At retail it can be bought at from 3 to 5 cents, according to the quantity obtained. One pound of acid is sufficient for fourteen tests. In a factory where acid is purchased by the carboy, it should not cost more than one-fifth cent per test, and in no case should it cost more than one-half cent per test.

The breakage of bottles, if properly made, is so slight that it need not be considered. We have made upwards of two thousand tests, in which only fifty bottles have been used, and only one of these bottles has been broken. The chemicals do not act upon the glass, and the bottles are only broken by accident or careless handling.

Cleaning the test bottles.—The bottles should be emptied while hot and afterwards rinsed twice with hot water; they are then ready for another test. In emptying the bottles they should be inverted and given a circular motion, which causes the liquid to form a whirlpool and allows air to enter continuously in the center of the tube; in this way the bottles may be emptied and cleaned rapidly without leaving fat attached to their sides.

Further precautions.—The sulphuric acid used should be kept out of reach of all persons except those making the test, and great care should always be taken in handling it as it is very corrosive.

If the fat does not separate clear from the acid liquid when water is added to bring it into the neck, it indicates that the acid used is too weak and more should be used. If the fat separates clear from the acid, but is blackened, it shows that the acid is too strong, and it should be diluted to a specific gravity of 1.82 before using, or a little less of the acid could be used for the test.

It sometimes happens in testing buttermilk that is quite sour, that the addition of water to bring the fat into the neck of the bottle where it can be measured causes a precipitate of casein or other matter, which mingles with the fat and prevents an accurate reading. This difficulty has also occurred a few times with milk that had stood a considerable time before testing; it may be entirely avoided by filling the bottles with a hot mixture of equal parts of sulphuric acid and water instead of water alone.

The greatest source of error is in the graduation of the tubes, and no one should purchase tubes except from reliable parties who will guaranty their accuracy.

The apparatus is now supplied in several sizes by Messrs. Cornish, Curtis & Greene, Fort Atkins, Wis.

The average differences between the results of twenty-nine comparative analyses made both by this method and by the gravimetric method is 0.08 per cent. The maximum differences are + 0.20 and — 0.16 per cent.

In Bulletin No. 19, new series, New York Experiment Station, June, 1890, tests are reported of Parsons's method of determining fat in milk (first annual report New Hampshire Experiment Station). The results differed too widely from those obtained by the gravimetric method. But when 15 cubic centimeters of soda solution and 10 cubic centimeters of alcoholic soap solution were employed, the agreement with the gravimetric method was satisfactory. A minute description of the apparatus and details of the method is given *loc. cit.*

Penney (report Delaware Experiment Station, 1889, 168) reports tests of the efficiency of the lactocrite and Cochran's method of determining fat in milk, comparing each with Soxhlet's areometric method. The results of twenty-two trials with the lactocrite show extreme deviations from Soxhlet's method of — 0.8 per cent and + 0.7, the mean deviation being 0.3. Thirteen out of twenty-two trials agreed fairly well with the standard.

Manns (Illinois Experiment Station, Bulletin No. 9) compares the results obtained by Short's method of determining fat in milk with the "gravimetric" method. In sixteen trials the average per cent of fat by the gravimetric method was 3.71; by Short's method, 3.78, and by a lactoscope method, 3.65. The extreme variations by Short's method were + 0.23 and — 0.22 per cent. By the lactoscope method, + 0.44 and — 0.53.

He also compared the pounds of butter fat found by Short's method in the milk supplied by a considerable number of dairy patrons with the pounds of salted butter obtained by the churn. The average difference between the two methods was 1.41 per cent of the quantity found by Short's test. The widest deviations were + 5.96 and — 3.85 per cent. He concludes that the Short method is trustworthy, and gives results agreeing quite well with the actual churn yield. It could well be used as a standard test in paying for milk by its actual butter value.

Farrington (Illinois Experiment Station, Bulletin No. 10) made a number of comparisons of the gravimetric method of determining fat, with the methods of Short, Parsons, Failyer & Willard, Cochran, and Patrick. The results were as follows:

	Gravimetric method.		Patrick.	Cochran.	Short.
	On sand.	On paper.			
Herd milk	.....	.....	3.12	.....	.....
	.....	.....	3.05	.....	.....
	3.09	.....	3.08	.....	.....
	3.11	.....	3.00	.....	.....
Average	3.09	.....	3.06	.....	.....
One cow	4.59	.....	4.50	4.67	.....
	4.46	.....	4.80	4.50	.....
Average	4.52	.....	4.65	4.58	.....
One cow	3.70	3.60	3.70	3.60	.....
	3.77	3.78	3.70	3.76	.....
	4.33	4.28	4.20	4.15	.....
	4.78	4.80	4.70	4.67	.....
	4.13	4.06	4.10	3.97	.....
Do	.....	.....	4.60	.....	4.78
	.....	.....	4.55	4.50	4.88
	4.69	4.58	4.69	4.55	4.88
	4.71	4.59	4.60	4.67	4.83
Average	4.70	4.59	4.59	4.57	4.85
One cow	.....	.....	4.00	3.97	3.86
	3.88	3.96	4.00	4.15	3.97
Average	.....	.....	4.00	4.03	3.91
One cow	.....	.....	4.20	4.15	4.68
	4.30	4.40	4.20	4.15	4.58
Average	.....	.....	4.20	4.15	4.63

	Gravimetric method.		Patrick.	Cochran.	Short.
	On sand.	On paper.			
Skim milk:					
Laboratory No. 234	0.57	.....	0.80	0.69	.....
	0.62	.....	0.80	0.69	.....
Average	0.59	.....	0.80	0.69	.....
Laboratory No. 241	0.48	0.48	0.60	0.48	.....
Laboratory No. 242	0.66	.....	.....	.....	.....
	*0.68	.....	0.70	0.69	.....
Laboratory No. 250	.....	0.94	.....	.....	.....
	0.94	0.97	0.80	0.79	.....
Laboratory No. 252	.....	.....	1.40	.....	1.12
	.....	.....	1.30	1.27	1.12
	1.23	1.28	1.30	1.38	1.12
	1.52	.....	1.30	1.27	1.12
Average	1.38	.....	1.32	1.31	1.12
Laboratory No. 261	.....	1.88	1.90	1.90	1.88
Buttermilk:					
Laboratory No. 235	0.37	.....	0.00	.....	.....
	0.37	.....	0.00	0.34	.....
Laboratory No. 239	.....	.....	0.00	0.00	.....
	0.46	0.47	0.35	0.32	.....
Laboratory No. 249	.....	0.87	0.00	0.00	.....
	0.81	0.90	0.60	0.93	0.80
Laboratory No. 253	.....	0.39	0.20	0.34	.....
	Lost	0.40	0.20	0.34	.....
Laboratory No. 258	.....	.....	0.50	.....	.....
	.....	0.96	0.50	0.69	0.40

*Asbestos.

Lezé (Compt. rend., 1890, 110, 647; abstr. Chem. Zeitg. Repert., 1890, 109) determines fat in milk as follows:

Into a flask with a narrow neck graduated to tenths of centimeters, bring 100 parts of milk and 200 to 250 parts of pure concentrated hydrochloric acid. Heat till the solution is brown and add dilute ammonia till it clears. Then fill the flask with hot water till the surface of the liquid is at the 0 mark on the scale and then read off the volume of the fat. Since fat at its melting point has a specific gravity of 90, the volume is to be multiplied by this factor to obtain the weight.

Gorodetzsky (Aus dem städtisch. Untersuchungslab. von Prof. A. Werigo zu Odessa, abstr. in Zeitschr. f. angewand. Chem., 1890, 418) has made twenty-nine analyses of milk for the comparison of Röse's method of determining fat with the usual sand extraction method and in some cases with Soxhlet's areometric method.

The author found five hours' time sufficient in nearly every case for the extraction of fat by the sand method; three hours' time was in many cases insufficient.

The comparison of the sand method, Röse's method, and the areometric method is given as follows:

Differences between the several methods.

	Röse's and sand method.			Sand and areometric method.			Röse's and the areometric method.
	Time of extraction.			Time of extraction.			
	3 hours.	5 hours.	7 hours.	3 hours.	5 hours.	7 hours.	
Maximum	+0.195	+0.195	+0.128	+0.112	+0.112	+0.115	+0.212
Minimum	−0.022	−0.060	+0.020	−0.053	−0.022	−0.021	+0.015
Average	+0.079	+0.037	+0.068	+0.017	+0.050	+0.015	+0.081

The experiments were apparently conducted with the greatest care, and the author gives particular description both of the methods and of the manipulation.

F. Walls (Chem. News, 61, 162) proposed a method of determining fat in milk, in which a tube containing asbestos is substituted for Adams's paper coil. The method does not differ essentially from the one proposed and used by Babcock.

F. Ballario and C. A. Revelii (Le Staz. Speriment. Agrar. Ital., 18, 113 ; Abstr. in Vierteljahresschr. Nahrungs u. Genussmittel, 1890, 5, 20) have made a long series of experiments to test the methods of fat determination by the lactobutyrometer and determination of solids by reckoning from the specific gravity and fat.

(1) *Determination of fat.*—Girard's method of using the lactobutyrometer was adopted, except that 20 cubic centimeters of alcohol ether-ammonia mixture were brought into the instrument first, and 10 cubic centimeters of milk were quickly added and shaken. The readings were made at 20° C. In reckoning the fat, both the tables of Tollens and Schmidt and those of Marchand were tested. The results were compared with those by Soxhlet's areometric method. The authors conclude that the instrument, used according to their directions, will give accurate results with milk containing between 1.3 and 4.5 per cent of fat.

(2) *Determination of total solids.*—The authors again call attention to the fact that the milk must be kept in a refrigerator, 6° to 8° C., for about sixteen hours before attempting to determine the specific gravity, then brought to a temperature of about 20° C. and the specific gravity determined.

The solids were determined by drying 5 cubic centimeters in a platinum dish without the addition of sand, to constant weight, which usually required three hours. Better agreement between the solids calculated and found was obtained by the use of Fleischmann and Morgen's formula than by using Fleischmann's newer formula. The authors find that the per cent of solids calculated agrees sufficiently with that analytically determined, and that neither skimming nor watering the milk renders the method less accurate.

J. C. Shenstone (Analyst, 13, 222) describes in detail his method of determining milk sugar and cane sugar in condensed milk. This has already been outlined in the Proceedings of the Sixth Annual Convention of Association of Official Agricultural Chemists, 1889, page 149.

Sugar determination in milk.—M. Kühn (Milch Zeitg., 1889, No. 47,925) has compared the methods of Tollens, Soxhlet and the polarimetric method (precipitation of the proteids) with acetic acid and sugar of lead as modified by Schmöger or with phospho-tungstic acid.

In using Tollens's method he employed 100 cubic centimeters of the sugar solution, 30 cubic centimeters water, and 40 cubic centimeters of Fehling's solution, boiled six minutes in an Erlenmeyer flask, filtered on asbestos, and reduced the copper oxide in hydrogen. Cu $\times 0.763$=sugar. In using Soxhlet's method he followed Fres. Quant. Anal., 6 Aufl., II Bd., 691; boiling for six minutes and then proceeding as above.

In using the polarimetric method, casein was first thrown down by acetic acid, and in the filtrate the remaining proteids were precipitated with sugar of lead or with phospho-tungstic acid.

The averages of twenty-one different analyses by the several methods are as follows:

	Per. cent.
Tollens	4.596
Soxhlet	4.623
Polarimetric:	
Using sugar of lead	4.679
Using phospho-tungstic acid	4.768

The results by the phospho-tungstic method were in some cases very considerably higher than by the other methods. The author holds in opposition to Schmöger that the phospho-tungstic method is not the most reliable, and for the present holds to Soxhlet's, Tollens's method requiring more time for its execution.

Cochran's method.—As the right to use this method is claimed to be covered by a patent, it is not further noticed here. The patentee will doubtless give all necessary particulars.

REPORT ON DAIRY PRODUCTS.

The following report relates exclusively to butter, and concerns only the determination in it of water, fats, casein, salt, and other mineral matters. It is designed to supplement the coöperative work of the association last year, which consisted in determining the volatile acids, specific gravity, melting point, etc., of butter fats; data which serve to detect the presence of foreign fats in butter.

It is very clear that a strict comparison of the "butter records" of individual cows or herds can only be made when the composition as well as the gross weight of the butter yield is known.

A cow that is giving in a fixed period 20 pounds of butter which carries 15 per cent of water is making a better "record" but is not producing as much butter fat as another cow that gives 19 pounds of butter in the same period with 9 per cent of water. When butter is worked honestly and carefully the water content of different churnings will vary considerably, and with a little manipulation can be made to hold from 15 to 18 or 20 per cent of water. A uniform and accurate method of butter analysis is therefore highly desirable.

The subject seems to have been rather slighted by writers on agricultural analysis, and some of the methods proposed in standard works could certainly never have been successfully used by their authors or any other man.

Grandeau (Traité d'Analyse des Matières Agricoles, 12th ed., 1883, 175) directs to determine water by drying about 20 grams of butter in a test tube on a water bath or in an oven to a constant weight. Fat is determined by dissolving in ether the residue from the water determination, filtering on a warm filter and washing with ether. A fraction of the filtrate is evaporated, dried, and weighed. The insoluble residue left on the filter, consisting of casein, sugar, salt, and other mineral matter, is washed with water, the washings are evaporated to dryness and if this gives any residue insoluble in water it is added to the contents of the filter, which are then dried, weighed, and incinerated. The difference in dry weight of the residue before and after incineration represents the casein. In the aqueous solution the total mineral matter, the sugar (by titration), and the salt are determined.

Böckmann (Chemisch-technische Untersuchungsmethode, II, 608) prefaces the details of his method of analysis with the remark that it presents no difficulty. Water is determined in 50 to 80 grams by heating at 100° to 110° till constant weight is secured, and fat is determined by extracting from 5 to 6 grams of the dried butter in an extraction apparatus. The residue from the extraction is collected on a weighed filter, dried, and weighed. It is then incinerated in a weighed platinum dish. Casein and milk sugar are thus determined by difference, and mineral matter by direct weighing. If the sugar is to be determined another portion of the dried butter is extracted with ether and the residue washed with water slightly acidulated with acetic acid on a weighed filter. Milk sugar is dissolved while casein and part of the mineral matter remains. This is dried and weighed on the filter. After incineration the weight of the ash is determined and deducted, thus giving the casein by loss of weight. Milk sugar is determined by subtracting the quantity of casein found in this operation from the sum of milk sugar and casein previously obtained.

Fleischmann, (Molkereiwesen, 588) weighs from 5 to 10 grams of butter into a small weighed beaker and after melting decants the clear fat into a weighed filter and funnel, receiving the filtrate in a weighed flask. All these vessels with the fat are dried at 100° C. and water is calculated from loss of weight. The residue is then brought into the filter with ether and washed till the fat is completely extracted. After distilling off the ether the flask with the fat is dried and weighed.

Mineral matter is determined by incinerating the residue left on the filter. From

100 grams of butter the fat is extracted and a nitrogen determination in the residue gives by calculation the quantity of casein.

These abstracts give a fair idea of the methods at present recommended for the analysis of butter.

WORK OF THE ASSOCIATION, 1889-'90.

PREPARATION OF THE SAMPLE FOR COÖPERATIVE WORK.

The method of preparing the sample is essentially that practiced by Mr. Babcock, of the Wisconsin Station. The sample which was sent to members of the association was fresh Connecticut creamery-made butter. A pound of this butter was heated slowly in a closed pint jar till just melted, then shaken violently for some minutes and quickly poured into tubes closed at one end with corks. These tubes were at once stoppered, brought to a cool place and kept in motion (turned end over end and also on their longer axes) till the butter solidified, which required only a few minutes. All the constituents were then determined in duplicate in the first tube filled, and single determinations were also made in the tube filled last, with the following results:

	First tube.			Last tube.
	1.	2.	*Average.*	
Water, 1¾ hours at 100° C	12.94	12.82	12.88	12.90
Water, 4 hours at 100° C	12.96	12.86	12.91	12.92
Casein and ash	6.46	6.48	6.47	6.49
Casein	1.39	1.34	1.36	1.27
Ash	5.07	5.14	5.11	5.22
Salt	5.00	5.11	5.05	5.23
Fat			80.62	80.59

These figures indicate that the contents of the tubes were nearly if not quite uniform in composition.

The tubes were then sent to a considerable number of stations, those being selected which were believed to be most engaged in dairy work. With each sample was also sent a proposed scheme of analysis with the request that the sample should be analyzed by that method and also for comparison by any other which seemed to the analyst preferable.

Following is the scheme:

PROPOSED METHOD OF BUTTER ANALYSIS.

To remove from the tube portions of the sample herewith sent for analysis, remove both corks and insert at one end a smaller cork that will readily pass through the tube. By pushing this with a rod the cylinder of butter is pressed out at the other end and may be cut off as wanted.

Water.—About 2.5 grams, accurately weighed, are dried in an air-bath at the temperature of boiling water until constant weight is secured. The dish used for the purpose must have a flat bottom of 3 or 4 square inches surface.

Fat, casein, and ash.—The dried butter from the water determination is treated in the dish with 76° benzine and stirred till the lumps disappear. The contents of the dish are then transferred, with the aid of a wash bottle filled with benzine, to a weighed Gooch crucible and washed till free from fat. The crucible and contents are dried at 100° for two hours and weighed. This weight, less the weight of the crucible, represents the casein and ash; and the difference between this and the dried butter represents the butter fat. The crucible is then ignited carefully, below a red heat, and weighed again. The loss in weight represents casein, the remainder mineral matter, chiefly salt.

RESULTS OF ANALYSIS.

One or two tubes broke in transit and several chemists were unable to do the work requested. In the following table are arranged the results obtained by eleven different chemists in nine laboratories.

The following chemists participated in the work: Maine Experiment Station, Messrs. Jordan, Bartlett and Merrill; Cornell Experiment Station, Mr. W. P. Cutter; Illinois Experiment Station, Mr. E. H. Farrington; Texas Experiment Station, Messrs. H. H. Harrington and W. Wipprecht; Wisconsin Experiment Station, Mr. S. M. Babcock; Kentucky Experiment Station, Messrs. W. A. Scovell and A. M. Peter; U. S. Department of Agriculture, Mr. Aug. E. Knorr; Pennsylvania Experiment Station, Mr. G. L. Halter; Connecticut Experiment Station, Mr. A. L. Winton, jr.

	Maine Experiment Station.		Cornell Experiment Station.	Illinois Experiment Station.	Texas Experiment Station.		Wisconsin Experiment Station.	Kentucky Experiment Station.	U. S. Department of Agriculture.	Pennsylvania Experiment Station.	Connecticut Experiment Station.
	B.	M.			H.	W.					
	Dup.	*Dup.*	*Dup.*				*Dup.*	*Dup.*	*Dup.*	*Dup.*	*Dup.*
Water	12.86	12.71	13.02	12.86	12.64	12.71	12.79	12.78	12.76	12.72	12.88
Casein	1.30	1.11	1.95	1.32	.88	1.12	1.18	1.26	1.37	1.49	1.37
Fat	80.80	81.08	80.02	80.75	81.90	81.51	80.96	80.93	†81.14	81.07	80.64
Ash (salt)	5.04	5.10	5.01	*5.03	4.58	4.66	5.07	5.01	4.73	4.67	‡5.11
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	99.98	100.00	99.95	100.00

	A.	B.	C.	D.
	Dup.		*Dup.*	*Dup.*
Water	12.80	[12.80]	12.86	12.83
Casein	1.07	1.24	1.50	1.56
Fat	81.02	80.76	80.68	80.37
Ash (salt)	5.11	5.09	‡4.97	5.24
	100.00	99.89	100.01	100.00

* 4.94. † 5.05. ‡ 4.95.

NOTES BY ANALYSTS.

Mr. Scovell could not get a constant weight in less than five and one-half hours when he used *round*-bottomed dishes 3 inches in diameter.

Thus the loss of moisture in two hours was 6.4 per cent; in three hours 8.4; in three and one-half hours 11.1; in five and one-half hours 12.7.

When he substituted a *flat*-bottomed dish 1½ inches in diameter, two hours' drying sufficed.

Mr. Scovell also determined water by weighing the butter into a weighed dish containing asbestos and drying at 105° C. in an oil oven to constant weight. The contents of the dish were then transferred to a Soxhlet's apparatus and extracted with Squibb's ether, and the fat was dried at 100° to constant weight. Another portion was washed with hot water several times and salt determined by standard silver solution (analysis A in the table). In another sample the asbestos, after extraction of fat, was returned to the dish, carefully dried at 105°, and reweighed, and thus fat was determined by difference; casein was determined by loss on subsequent ignition and ash from the residue. (Analysis B in the table.)

Mr. Jordan reports that in the water determination three and one-half hours' drying were necessary to secure constant weight.

Mr. Cutter reports the drying as tedious. He prefers to use sand to absorb the butter for drying, determines ash in a separate portion, and casein by difference, or by a nitrogen determination by the Kjeldahl method.

Mr. Farrington found that the shape and size of dish made a great difference in

the time required for evaporation of the water in butter, and he got a constant weight quickest by using asbestos in the dish with the butter. Using ether instead of benzine for dissolving the fat (otherwise following the proposed method), he got the results given in Analysis C.

By extracting the residue left on asbestos, after determining water in a Soxhlet extractor and weighing the extracted fat, he got in duplicate determinations 80.47 and 80 per cent of fat, while by the indirect determination he got 80.75 and 80.68 per cent.

Mr. Babcock prefers to dry the butter on asbestos, extract the fat and weigh it directly. He states that the direct weighing gives him on the average 0.25 per cent more fat than the indirect method. He says: "I at first supposed that this difference was due to ether remaining in the fat, but do not think so now. I have added ether to pure butter fat, and after evaporating it in the same way as in my analyses have found the weight practically the same as at first. The error due to oxidation of fat while drying is very slight. In butter and milk analysis we dry the fat in a vacuum oven under diminished pressure. This greatly diminishes the time required and gives more uniform results. The fat-free residue from either butter or milk appears to be either quite hydroscopic or easily oxidized, as results by difference rarely gave as close difference as direct weighing, while with me they have been uniformly lower." He determines ash in a separate portion and curd by difference. Where curd is determined by N × 6.25 he always finds from 0.2 to 0.5 excess (over 100 per cent). An analysis made in this way is marked D in table.

At the Connecticut Station, in numerous tests, Mr. Winton found the method of drying without sand or asbestos at 100° in an open dish perfectly satisfactory, *provided the surface exposed was sufficient* and the layer of butter not too deep. A surface of 3 to 4 square inches for 2½ grams of butter made it possible to complete the drying in two hours.

It has been proposed to weigh casein and ash together after removing water and fat as follows: The butter in a weighed Gooch crucible is placed in the water bath on bibulous paper. The water evaporates and at the same time the fat is drawn out by the blotter. It then only needs a slight washing with benzine to remove the last traces of fat, and casein and ash alone remain. Working in this way Mr. Winton got casein and ash 6.22 and 6.26, instead of 6.46, 6.48, and 6.49 by the other method. The casein was 1.28 and 1.31, instead of 1.34, 1.39, and 1.27 by the other method. Here is a loss of 0.23 per cent, falling chiefly on the ash, and due no doubt to the fact that water also passes out to the blotter with the fat, carrying salt with it.

Mr. Winton found no advantage in using sand in the determination of water.

Thus, when dried without sand for two hours the sample lost 12.77 per cent of water; when dried with sand for the same time it lost 12.80 per cent. If the dishes used are too small or of unsuitable shape, the addition of sand or asbestos facilitates drying.

The following additional water determinations were made, all in platinum dishes of the size and shape recommended in the scheme of analysis.

Temperature 100°, time of drying one and three-quarter hours, per cent of moisture 12.94, 12.82, and 12.90. Temperature 100°, time of drying three hours, per cent of moisture 12.96, 12.86, and 12.92. Temperature 105°, time of drying two hours, per cent of moisture 12.77. Temperature 105°, time of drying two hours, per cent of moisture 12.77.*

DISCUSSION OF THE RESULTS.

The average of all the analyses made by the prescribed method is as follows:

Water	12.79
Casein	1.31
Fat	80.99
Ash	4.91
	100.00

*Dried with sand.

Water.—The extremes in the several determinations of water differ by 0.38 per cent. Two out of the eleven differ from the average of all by more than 0.15 per cent.

Casein.—The extreme difference between the several determinations is 1.07 per cent, and five differ from the average, by more than 0.15 per cent.

Fat.—The extremes in the fat determination differ by 1.88 per cent. Six of these differ from the average of all by less than 0.20 per cent. Three others are not more than 0.5 per cent from the average, and three determinations are "wide."

Ash.—The extremes in ash determinations are 0.53 per cent apart. Five of them are within 0.15 per cent of the average, and three more are within 0.20 per cent.

The water determinations are quite satisfactory. It appears to your reporter doubtful whether, if the method and manipulation were faultless, results could be expected to agree much more closely than those herewith reported, considering the difficulty of preparing a sample for analysis which shall be perfectly homogeneous. The results are sufficiently close for any present demand. The extreme difference between the highest and lowest determinations would amount to a difference of only 6.4 ounces on 100 pounds of butter.

There is room for improvement in the determination of the other ingredients. The dangers which beset the method are:

(1) Volatilization of salt by overheating when casein is burned off.

(2) Mechanical loss at the same time by decrepitation of salt. The crucible should be covered when the heat is first applied.

(3) The residue, consisting of casein and salt, is said to be quite hygroscopic, and needs to be carefully dried and quickly weighed.

(4) If ether is used instead of benzine to dissolve the fat, it will dissolve part of the salt also unless the ether is perfectly anhydrous.

In conclusion your reporter recommends the adoption by the association of the following

METHOD FOR THE ANALYSIS OF BUTTER.

Sampling.—If large quantities of butter are to be sampled a butter tryer or sampler may be used. The portions thus drawn are to be perfectly melted in a closed vessel at as low a heat as possible, and when melted the whole is to be shaken violently for some minutes till the mass is homogeneous. A portion is then poured into a vessel, from which it is to be weighed out for analysis and should nearly or quite fill it. This sample should be kept in a cold place till analyzed.

Determination of water.—1.5 to 2.5 grams are dried to constant weight, at the temperature of boiling water, in a dish with flat bottom having a surface of at least three square inches.

The use of clean dry sand or asbestos with the butter is admissible, and is necessary if a dish with round bottom is employed.

Determination of fat.—The dry butter from the water determination is dissolved in the dish with absolute ether or with 76° benzine. The contents of the dish are then transferred to a weighed Gooch filter with the aid of a wash bottle filled with the solvent, and are washed till free from fat. The crucible and contents are heated at the temperature of boiling water till the weight is constant. The weight of the crucible and contents deducted from the weight of the dried butter gives the quantity of fat present.

Substitute method for fat.—Water may be determined by drying the butter on asbestos or sand, and the fat extracted by *anhydrous, alcohol-free* ether in an extraction apparatus. The extract, after evaporation of the ether, is heated to constant weight at the temperature of boiling water and weighed.

Determination of casein and ash.—The crucible containing the residue from the fat determination, consisting of casein and ash, is covered and heated gently at first, gradually raising the temperature to just below red heat. The cover may then be removed and the heat continued until the contents of the crucible are white. The

loss in weight of the crucible and contents represents casein, and the residue in the crucible mineral matter. In this mineral matter, dissolved in water slightly acidulated, chlorine may be determined gravimetrically with silver nitrate.

Mr. McDonnell asked what was meant by "76° benzine," referred to in the recommendation as to determination of fat.

Mr. Stubbs said that it meant benzine which flashed into vapor at 76°; that was the way he bought it.

Mr. Myers said that it was a commercial term.

Mr. Terne said that 76° Baumé was meant.

Mr. McDonnell said that he had not been aware that Baumé lighter than water ran up to 76°.

Mr. Wiley said that it did not run up; it ran down.

Mr. Stubbs said that he was rather certain about the meaning; that it was as he had stated. He used a great deal of benzine and gasoline, using gasoline whose flashing point was 77° and benzine that flashed at 76°. Kerosene oil flashed at 120°; he felt sure that the recommendation referred to the temperature at which the benzine vaporized and flashed.

Mr. Myers said that when he had received from Mr. Jenkins the samples of butter and directions for making the analyses he had been puzzled by the term "76° benzine," and had written to inquire its meaning. Mr. Jenkins had replied that it was a commercial term for a particular grade of benzine. The speaker did not now know, nor did he care, whether the reference was to the flashing point or to the specific gravity; the title under which the article was sold was "76° benzine."

The president said that his gasoline was purchased from the Standard Oil Company; he bought it from 76° to 87°, and tested it by Baumé to make sure that it was right.

Mr. Terne said that he bought three or four carloads a month, buying it all by degree of Baumé.

Mr. McDonnell said that, being puzzled by the point, he had looked through all his chemical books, but could find no degree of Baumé to correspond with 76.

Mr. Lupton moved that the report on dairy products, together with the method recommended by Mr. Jenkins for butter analyses, be adopted as read. Seconded.

Mr. Woods inquired why, in determining the specific gravity and in estimating the volatile acids, it was necessary or advantageous to rinse a flask with alcohol and ether.

Mr. Wiley said that the specific gravity flasks were presumed to have been used before, and it was difficult to clean the fat out of such flasks with water. Ether and alcohol would remove the bodies insoluble in water, and after being washed with these the flasks could be dried more easily; the alcohol removed any water which might have been left in the flask, and the ether removed any remaining alcohol, so that in

subsequent drying the whole would be clean. This was the reason for directing that the flasks be rinsed in alcohol and ether.

Mr. Woods said that he had deemed it a piece of unnecessary labor. After cleaning his flasks with soap and water he had tested them with alcohol and ether to see whether anything more would come out; he had failed in both cases, the flasks weighing the same after the treatment as before. He had found no difficulty in cleaning with soap and water. The time and trouble involved in redistilling made it a considerable nuisance, and in the estimating of volatile acids and of specific gravity he had had, so far as he knew, no difficulty whatever.

Mr. Wiley said that it was quite difficult to remove soap from the inside of a flask if used to clean the flask; a good deal of water had to be used subsequently, and if the flasks were to be reweighed, some difficulty would be experienced in getting them dry.

Mr. Woods said that he found no difficulty in drying them out in an hour.

Mr. Wiley said that the flasks were sometimes wanted for immediate use.

Mr. Woods said that he did not understand the rinsing to be an essential part of the method.

Mr. Wiley said it was not; the direction was simply for the sake of convenience.

Referring to the report of Mr. Jenkins, in which of course he was very much interested, he was pleased to find the analyses so concordant. It seemed to him, however, that to call the method one for the analysis of butter was almost a misnomer, it being only a preliminary method to the analysis of butter.

The president said that he understood the intention was to adopt this report in connection with the last one upon the same subject.

Mr. Wiley said that the adoption of this, as a method for the analysis of butter, would eliminate some of the most important work which the association was called upon to do, namely, the distinguishing of natural from artificial butter; therefore, while he was perfectly agreed to the method recommended by the reporter for a *partial* analysis of butter, he thought it improper to call it a method for the analysis of butter, thereby implying that nothing else was to be done by the chemists of the association in butter analysis. He believed it would be proper to substitute the method proposed for similar methods in the old report, letting the rest remain for subsequent work and improvement.

The president said that there seemed to be no preliminary report; he thought that had been left out.

Mr. Cooke moved, as an amendment to the motion before the convention, that the report of Mr. Jenkins be accepted simply, the matter of adopting the method proposed to come before the association, part by part, in the regular order of business, following the plan carried out in regard to the report on nitrogen.

The president said that such a motion was unnecessary; the report was accepted by being read; its adoption was another thing.

Mr. Frear said that according to his understanding this method, if adopted, was to be used for the comparison of undoubted samples of butter, for instance, at prize shows, for the purpose of determining which cow would give the most butter; that it was not intended as a substitute for methods involving the determination of volatile acids, melting point, etc., and that this would be stated in the report.

The president said that he had taken it for granted that the present report was to be considered as an addition to the report of last year, which, containing nothing in regard to a preliminary examination of butters, went directly to their adulteration.

Mr. Lupton asked whether the report differed materially from that made last year by Mr. Wiley.

Mr. Wiley said that there was some difference in the method of estimating the salt; the proposed method was by difference in weight on ignition, which was evidently a less accurate method than the other; but the present report related principally to the sections printed on page 209 of the report for last year.

The president said that a motion to adopt the report was before the convention. A motion to substitute would be in order.

Mr. Cooke said that in the method of sampling it was stated to be necessary to keep the sample in motion while cooling after melting and pouring out; the final method should also contain that direction, for it was very essential that the sample should be shaken while cooling. It seemed somewhat strange that the association should have to adopt an indirect method for getting the fat, which was the principal thing, but the method proposed was one of indirect determination, getting the fat by difference. Any mistake in the water would make a mistake in the fat, and so would any error in the curd or salt. It would seem that the association ought to be able to find some direct method of determining the butter fat.

Mr. Farrington said that in his judgment, based upon butter analyses made by himself, the proposed method of estimating the fat was much more accurate and presented fewer difficulties in manipulation and weighing than that of extracting and weighing in large quantities. He hoped the method would be adopted.

Mr. Myers suggested that the recommendations be taken up seriatim in connection with last year's report, discussed one at a time, amended as might seem best, and then adopted as a whole.

There being no objection the president so ordered, and requested Mr. Wiley to read the recommendations in connection with the report of last year.

Mr. Myers moved that the method for microscopic examination of butter remain as it was last year (page 200). Carried.

Mr. Myers moved that the method for determining the specific gravity remain as it was last year (pages 200, 201). Seconded.

Mr. Wiley said that Mr. Knorr had made some very interesting determinations in connection with the matter of specific gravity relative to the weight of water in the flask compared directly with water at the same temperature.

Mr. Knorr said that what he had done was simply to calculate the weight of the water contained in the flasks at the temperature of 100° by the formula given in Landolt's chemical physical tables. Instead of filling the flask with hot water and allowing that to cool, he simply calculated the weight of the water.

Mr. Wiley said that comparisons had shown this method to be even more rapid than that of calculating the water contained in the flask at the temperature given from the table of constants for that purpose; a recalculation never had to be made, so that a great deal of time and labor was saved. He would like, if Mr. Knorr could put his method in shape for introduction, to have the method of last year amended so as to include it; it had been found fully as accurate as the method now in use, if not more so. A table could be inserted from which the calculation might be made for any flask.

Mr. Knorr said that it was a regular formula for calculating the weight of flasks or glass vessels.

Mr. Anderson asked whether difficulty would not arise from atmospheric differences; he had found that the weight of water differed from time to time.

Mr. Wiley said that the pressure of air was presumed to be reasonably constant. Of course with a very low barometer the water in the flask would boil at a lower temperature than with a very high barometer, for the latter would give a higher temperature and the weight of a given volume of water would be less; but the variations were so small as to introduce no appreciable error into the number for specific gravity, and, as they pertained equally to the water and the oil, the calculation made for any given locality was applicable except with a very low or a very high barometer; for all ordinary pressures they made no appreciable error.

Mr. Myers said that in this connection he would like to hear the recommendations of Mr. Jenkins in reference to determining the water.

Mr. Wiley said that the proposed amendment related only to the method for determining specific gravity, and had nothing to do with the determination of water in the butter.

The president said that he so understood.

Mr. Wiley said that the amendment proposed was the insertion, as an alternate method for determining the weight of water, its computation by the formula of Landolt.

The amendment was agreed to.

Mr. Myers moved that the method for determining the melting point remain the same as it was last year (pages 202–204). Carried.

Mr. Myers moved that the method for the estimation of volatile acids remain the same as it was last year (pages 204–207). Carried.

Mr. Myers moved that the method for determining iodine equivalent remain the same as it was last year (pages 207, 208). Carried.

Mr. Myers called for the recommendations of Mr. Jenkins.

Mr. Wiley read the first recommendation, as follows:

Sampling—If large quantities of butter are to be sampled a butter tryer or sampler may be used. The portions thus drawn are to be perfectly melted in a closed vessel at as low a heat as possible, and when melted the whole is to be shaken violently for some minutes till the mass is homogeneous. A portion is then poured into a vessel from which it is to be weighed out for analysis, and should nearly or quite fill it. This sample should be kept in a cold place till analyzed.

Mr. Wiley said that this was the point where Mr. Cooke suggested the insertion of the statement that the sample vessel also should be kept in motion until the butter was solidified. Evidently it was the idea of Mr. Jenkins that the whole sample should be taken.

Mr. Myers suggested that possibly some members of the association did not know what was meant by "butter sampler." It might be well to define it.

Mr. Wiley said that he generally used a case knife; he supposed that the sampler spoken of in the recommendation was something like the thing used in sampling sugars, a conical, hollow instrument with a slit in one side, which could be thrust into a mass of butter and withdrawn to remove a portion of it.

Mr. Cooke said that the hollow was in the form of a half circle.

Mr. Huston said that he had seen used for the purpose a brass tube cut in two lengthwise, leaving half the tube, the lower end of which was provided with a solid piece of brass flush with the cut; this made a very efficient instrument for sampling the material, the block in the end preventing any of it from slipping back.

The president said that as he understood the recommendation it was that from a large sample, taken by melting, a smaller sample was to be set apart for analysis by means of melting the butter at a low temperature.

Mr. Van Slyke inquired as to how many grams might be considered a large sample.

Mr. Wiley said that further back in the report the quantity was stated as about one pound.

A member said that it would be well to insert in the recommendation some approximately definite quantity; 10 or 20 grams might be considered a large quantity by some chemists and some might think 1 gram large.

Mr. Van Slyke said he would move that a certain number of grams be taken as the sample if some one would suggest the quantity.

Mr. Wiley suggested that about 500 grams would answer.

Mr. Van Slyke moved that 500 grams be inserted as the amount to be taken as a sample when that quantity of butter should be on hand.

Mr. Cooke asked whether it would be necessary to take the small sample from a large sample of 500 grams.

Mr. Lupton said that it might be well to make it from 100 to 500 grams.

Mr. Wiley said that the idea in saying *about* 500 grams was the impossibility of prescribing the exact amount of a sample in all cases. Amended as proposed, the recommendation would read:

If large quantities of butter are to be sampled a butter tryer or sampler may be used. The portions thus drawn, about 500 grams, are to be perfectly melted in a closed vessel at as low heat as possible, etc.

The amendment was agreed to, and the recommendation of the reporter, as amended, was adopted.

Mr. Wiley read the second recomendation, as follows:

Determination of water.—1.5 to 2.5 grams are dried to constant weight at the temperature of boiling water in a dish with flat bottom having a surface of at least 3 square inches.

The use of clean dry sand or asbestos with the butter is admissible, and is necessary if a dish with round bottom is employed.

Mr. Wiley suggested that the secretary be authorized to transform the 3 square inches into its equivalent in square centimeters, that the measure might be in conformity with the scientific standard. He said that the old method (page 209) differed from that now recommended; it required the use of clean dry sand and a temperature of 105°; the direction was to heat for two hours.

Mr. Myers moved that the suggestion be adopted. Carried.

Mr. Lupton asked whether the temperature was stated in the recommendation.

Mr. Wiley said that it was; the temperature was fixed at the boiling point of water, the standard temperature adopted by the association. Comparing Colorado with Louisiana, the difference in temperature would be very considerable, but the rate at which water went off from a substance depended generally upon the pressure and the temperature, and boiling water gave a constant condition everywhere, so that with that as a standard all worked under the same conditions although there was a difference in the actual temperature.

The recommendation, as amended, was adopted.

Mr. Wiley read the third recommendation, as follows:

Determination of fat.—The dry butter from the water determination is dissolved in the dish with absolute ether or with 76° benzine. The contents of the dish are then transferred to a weighed Gooch filter with the aid of a wash bottle filled with the solvent, and are washed till free from fat. The crucible and contents are heated at the temperature of boiling water till the weight is constant. The weight of the crucible and contents deducted from the weight of the dried butter gives the quantity of fat present.

Mr. Woods asked whether there was any way of knowing when the washing free from fat was accomplished.

Mr. Caldwell suggested that the solution be tested with nitrate of silver for chlorine.

Mr. Wiley said that would hardly do; in this case it was not chlorine

but fat that was to be washed out. Perhaps the best way was to take a drop on a platinum spatula, heat it, and see whether it gave off any fumes from the burning of organic matter. Each chemist could determine for himself whether all the fat was washed out; it was hardly worth while to encumber the method with that.

Mr. Cooke said that he thought some emphasis should be put on the word "absolute." Squibb's ether would not serve the purpose; the best ether made in this country would not answer for that requirement. Ether could be imported very cheaply; the imported ether could be brought here at from 63 to 65 cents a kilogram, which was very much cheaper than Squibb's ether, and would stand any of the tests he had tried.

Mr. Wiley said that the last sentence of the recommendation was evidently a clerical error. It said "the weight of the crucible and contents deducted from the weight of the dried butter gives the quantity of fat present." This was not so, for the weight of a crucible not there before had been introduced. The error could be corrected by substituting the statement that the weight of fat was calculated from the data obtained.

Mr. Myers suggested that either the secretary or the reporter should explain in a footnote the meaning of "76° benzine."

Mr. Huston said that it would be well to redistill the benzine; he had experienced considerable trouble with benzine, and he would bring up later the matter of its boiling points.

The president said that he had found in absolute ether something which had weight and was very explosive.

On motion, the recommendation was adopted.

Mr. Wiley said that the next recommendation contained a direct method; Mr. Cooke had said that there should be one. The fourth recommendation was as follows:

Substitute method for fat.—Water may be determined by drying the butter on asbestos or sand, and the fat extracted by anhydrous, alcohol-free ether in an extraction apparatus. The extract, after evaporation of the ether, is heated to constant weight at the temperature of boiling water and weighed.

Mr. Woods inquired whether any one present had tried the method in question; he had tried it without success.

The president said that he had tried the method and had reported the results, which were the same as by the other method.

Mr. Woods said that his results had sometimes been comparable, but sometimes they had not.

On motion, the recommendation was adopted.

Mr. Wiley read the fifth recommendation, as follows:

Determination of casein and ash.—The crucible containing the residue from the fat determination, consisting of casein and ash, is covered and heated gently at first, gradually raising the temperature to just below red heat. The cover may then be removed and the heat continued till the contents of the crucible are white. The loss in weight of the crucible and contents represents casein, and the residue in the cruci-

ble mineral matter. In this mineral matter, dissolved in water slightly acidulated, chlorine may be determined gravimetrically with silver nitrate.

The president asked if an alternate method was given; if the alternate were used for fat there would have to be one for the casein and ash.

Mr. Wiley said that no other method was given for casein and ash.

Mr. Myers moved to amend the recommendation by adding at the end thereof the words *or volumetrically.*

Mr. Wiley suggested the further addition of the words *using potassium chromate as an indicator.*

Mr. Myers accepted the suggestion.

The amendment was agreed to, and the recommendation of the reporter, as amended, was adopted.

Mr. Wiley said that it was often desired to determine only the salt in a butter. In that case the method given on page 209 would be found very easy of application, very accurate, and very quick. He had worked it hundreds of times, and knew it to be reliable. He moved that the method referred to be added as an alternate method for estimating salt. Carried.

Mr. Cooke moved that the Kjeldahl method be allowed as an alternate method for estimating the curd. Carried.

Mr. Myers said that it was frequently desirable to make other determinations, and that last year a series of elective determinations had been adopted and were incorporated in the printed method (pages 209-212); these methods seemed to be reliable. He moved their readoption as a whole. Carried.

Mr. Wiley said that the reporter had made no further recommendations. Beside butter there were other dairy products, but as to them no report was made by Mr. Jenkins; probably the association would do well to retain the methods of last year.

Mr. Voorhees said, referring to milk analysis, that he had made during the past year a long series of duplicate determinations, using the official method and the method of drying in a flat-bottomed dish. The results were very concordant; the average results of a very large number of determinations were almost identical with those obtained by the official method, and it was found that drying in flat-bottomed dishes without sand was very much more rapid and easier than the other way. He would like to see that method inserted either in place of the one now employed or as an amendment. He moved that the present method be amended as indicated.

Mr. Wiley said that the amendment could be easily made by inserting after the comma following the words "dry sand" (page 212) the words *or without sand.*

Mr. Voorhees said that the method did not mention a flat-bottomed dish; it was not necessary that the dish should be of platinum; nickel would answer.

Mr. Wiley said that the word "platinum" might be striken out and

the words *or without sand* inserted after the comma following the words "dry sand."

Mr. Myers asked how Mr. Voorhees got rid of the thick covering of albumen which formed and dried.

Mr. Voorhees said that he did not try to get rid of it; he got the water out of it, it mattered not how.

Mr. Myers said that in West Virginia it would not get out.

Mr. Voorhees said that it did in New Jersey.

Mr. Wiley suggested that probably that was owing to the tendency everything had to get out of New Jersey.

Mr. Huston said he was not certain but that the method should prescribe a metallic dish of some kind; he had no experience upon the point, but thought that if platinum worked well something more should be known in regard to the matter before permitting the use of a dish made of porcelain, glass, or any other material less suitable than metal. It would be safe to say a metallic dish.

Mr. Woods said that he had repeatedly used a porcelain dish with sand, but never without it.

Mr. McDonnell said that he saw no reason why a glass dish should not be used; he had used a flat glass dish in drying butter and it worked very well; not having a flat platinum dish, he had taken the bottom of a flat beaker, and that answered every purpose.

Mr. Frear said that open capsules with flat bottoms served the purpose and dried very well.

Mr. Wiley said that he thought it perfectly safe to say simply *a flat dish;* then if a chemist found that one kind of a flat dish would not answer he might use another.

The amendment was agreed to, and on motion the method for determination of water, as amended, was adopted.

Mr. Voorhees, referring to the method for total nitrogeneous matter, inquired whether it was necessary to evaporate the milk to dryness. The method said:

> Evaporate to dryness in the Kjeldahl digestion flask a known weight (5 grams) of milk and proceed exactly as described for this method by the nitrogen reporter.

It had not occurred to him that it was necessary to evaporate to dryness if a good digestion could be had without that.

Mr. Wiley said that "dryness" here meant only smaller bulk; the evaporation was to be continued until the sample was thick.

Mr. Voorhees moved that the method be so amended as to prescribe that the Kjeldahl determination be made directly without evaporating to dryness. Seconded.

Mr. Wiley asked whether Mr. Voorhees had made determinations in that way, and had found them perfectly reliable.

Mr. Voorhees said that he had made three or four hundred such determinations, and they were perfectly satisfactory.

Mr. Van Slyke said that in the Geneva laboratory the plan of Mr. Voorhees had given most satisfactory results.

Mr. Cooke said that in his laboratory the sulphuric acid was put in without evaporating to dryness.

The motion was carried.

Mr. Wiley said that had he been a reporter on dairy products for the present year he should have recommended among the methods for fat estimation some of the commercial methods which had been brought into general use by Babcock, Patrick, and Parsons, and which had evidently proved successful. As it was, he had not kept track of the method during the past year, and therefore had nothing to offer further than to say that certainly the methods referred to might be included as alternate methods for the estimation of fat. He was inclined to believe that those methods were accurate, even for chemical purposes, and would like to know whether the members of the association had had experience with them.

Mr. Caldwell said that he had procured the apparatus and made a thorough trial of the commercial methods in his laboratory; he had found them all very nearly alike, and all very satisfactory methods for general use. He had not carried the experiment so far as to enable him to make a statement as to their comparative accuracy and convenience, but had selected Cochran's method as the one that seemed to him the most convenient of all.

Mr. Kedzie said that he had used the Patrick method and found that parallel samples determined by that method and by extraction with ether ran closely together, the differences being very trifling. The great difficulty with the Patrick method was that after using the tube a few times the rubber became leaky and the material spurted out on the fingers of the analyst, spoiling both the experiment and his temper; otherwise it answered very well.

Mr. Frear said that in his laboratory the Cochran and Short methods had been tested; the former had given satisfactory results; in using the latter he had occasionally found wider differences, and there was difficulty in securing complete saponification; otherwise it was all right. In the Cochran method there was no saponification to take place and very good results were obtained.

Mr. Farrington said that he read Mr. Caldwell's published work about a week before he was ready to publish his own report on the methods in question; he tried all the volumetric methods he could find in print. He thought that the methods of Babcock, Patrick, and Cochran could be relied upon for the determination of the fat as well as any of the gravimetric methods, and he moved that descriptions of the three methods named be printed in the proceedings of the association. Seconded.

Mr. Wiley said that the methods of Patrick, Parsons, and Short were published in last year's Bulletin on pages 163, 164, and 166, respectively. They were not given in the methods, because he had had no opportunity to test them. The other methods referred to had not

appeared at the time of publishing the bulletin. He thought Mr. Farrington's motion was a good one, and as the methods then just published were printed in the report of last year it might be well this year to describe the methods of Babcock, Patrick, and Cochran without adopting them. From what he had read he deemed these three the best of the methods proposed.

Mr. Cooke said that in his laboratory a method for milk analysis was used which had been published some time ago but had not yet come into general use; in fact, very few had ever heard of it. This was known as the "Beimling centrifugal milk test," and was really the application of the lactocrite to a simple and cheap hand machine. More than a thousand tests had been made with it in his laboratory, and he was so well pleased with it that probably within the next six months he should adopt it for use in analytical experiments requiring the utmost accuracy, in place of the Adams method, which he now employed.

Fifteen cubic centimeters of milk are put into a test bottle with a neck graduated to read per cent of fat direct, 3 cubic centimeters of half-and-half rectified amyl-alcohol and concentrated hydrochloric acid added and mixed with the milk by shaking, and the test bottle filled with oil of vitriol, the whole being mixed by shaking. The bottle is then whirled in the centrifuge for half a minute. The casein is entirely dissolved and the fat collects in the melted state, pure and perfectly free from all water, casein, etc., within the graduation of the neck, from which the per cent of fat may be directly and accurately read.

In regard to the accuracy of the method, he would say that one of the students, who was not a chemist, was set to work with the machine, and on the second day he made 24 determinations, 75 per cent of which came within one-tenth of 1 per cent of the results by the Adams method. Theoretically a machine should give more accurate results than the Adams method, or any other of the long methods, for it very largely reduced the personal equation. The whole operation on a single milk need not take more than three minutes, and twenty-five determinations an hour could be made by anyone of ordinary manipulative skill.

Mr. Penny said that he would like to ask whether the association desired to advertise a method already patented. The method of Cochran was manufactured and sold under a United States patent, and on that ground it did not seem exactly right to recommend it. He had had an opportunity of testing it when operated by the inventor, and comparing it with the gravimetric method. It operated very well, but was liable to occasional slips, for which no good reason could be assigned. He had also had an opportunity of comparing the method in the hands of a practical dairyman. Although it gave good results, he should regret to see it given a place in the proceedings of the association, for it was not a scientific method.

Mr. Myers said that he agreed with Mr. Penny in thinking that the association should not adopt patented inventions. When a man did

scientific work for the benefit of the public it ought to be brought forward. He objected very seriously to the incorporation of Cochran's method as a part of the system adopted. If chemists wished to use it, well and good.

The president said that the motion was simply to describe the method.

Mr. Myers said, that while the matter was one that each chemist would have to settle for himself, he very strongly disliked the tendency of investigators to patent methods. It was all right for a man to patent a piece of machinery if he could make anything out of it, but to patent a method of analysis was different. In his own laboratory, during the past year, some two thousand five hundred or three thousand analyses of milk had been made, comparing the methods of Short, Patrick, Adams, and the lactocrite. It was sometimes difficult to get accurately graduated tubes for either the Patrick or the Short method, but if proper care were taken and correct tubes selected these methods were to all intents and purposes equally accurate with the Adams method, or any of the older methods, and as the association was engaged in a work that would extend very largely to the experiment stations, the demands of workers in those stations should be considered in the adoption of methods. A man in an experiment station frequently needed the ability to make a great number of analyses in a short time; the same was true of persons who tested milk in the health departments of the cities; and where there was an accurate and thoroughly reliable mechanical method, like the one published by Babcock, or a quick method like Short's or Patrick's, he thought the association should use it. These methods were cheap, quick, and arrived at satisfactory results. He thought that the association would do well to adopt them, in a measure at least, in a qualified way, so that they should receive official recognition.

Mr. Caldwell said that he did not quite like the motion as it stood. He did not know why there should be no mention of the Parsons method, of which something could be said that he thought could not be said of the others. He considered it certainly superior to Patrick's method, in which the heating tube was, he believed, objectionable. He doubted whether it was worth while for the association to put its seal upon any of these methods at the present time, or to bring any one of them into prominence, all of them being on somewhat the same principle, without a more careful examination and testing; to do so would not be quite fair. The method mentioned by Mr. Cooke was entirely different in principle; but even that, he thought, ought to be tested, and it seemed to him that the association should proceed somewhat cautiously before recommending any one of the methods in question.

Mr. Farrington said that he had intended no unfairness in omitting mention of the Parsons method in his motion, which was simply to include in the proceedings of the association descriptions of new methods along with those already described.

The president said that, as he understood the motion, it was simply

that the methods referred to should be published in the bibliography as methods which had come out during the year, and without any recommendation.

Mr. Lupton said that it did not seem right to publish with the scientific methods of the association practical methods which were merely applications of principles, and all of which were, as he believed, patented. He would have the association remember that its proceedings were before the scientific world, and as for himself he wished to keep away from patents altogether, and doubted the propriety of publishing patented methods in the way proposed. Any chemist who wished to use or test these methods could get them.

Mr. Wiley asked whether any of the methods in question other than Cochran's had been patented.

Mr. Caldwell said that Cochran's method was the only one patented.

Mr. Lupton said that Short's method was used by dairymen, and he thought that something about it—probably the tubes—had been patented.

Mr. Wiley said that for his own part he should be opposed even to the publication in the bulletin of any method of analysis which was covered by a patent, as being outside the range of scientific investigation, and as the members of the association professed to be scientific men. There was, however, nothing in the laws of the United States prohibiting chemists from using any method they pleased, patented or unpatented, in their own laboratories. No patent law could prevent a chemist from estimating fat in any way he chose so long as he did it in the line of scientific research and not for gain, and similarly he might use any method for determining any substance. Nevertheless, the publication of a method was a recommendation, and he should much prefer to have the association omit Cochran's method and publish an account of the others in addition to those already inserted.

Mr. Caldwell said that he was in full sympathy with the opinion expressed by Mr. Wiley. When Cochran published his method in the Journal of Analytical Chemistry it was already patented, but the inventor did not say anything about that, and the speaker did not know it until after he had gone over the matter very carefully, which he did, being thus caught in a trap as it were.

Mr. Frear said that the method might be stated as a patented one. It was widely used in the Pennsylvania creameries, and the creamery men ought to have some statement as to its accuracy. So far as scientific investigation was concerned, he thought that Cochran had no idea of making gain from the method; but being used for gain as a commercial process in a large number of establishments, he had probably felt that it would be fair for him to receive a small share of the profits accruing to the creamery men from its use. It was not apparent that such an extension of patents to methods was foreign to scientific ideas; the method was not advocated for scientific, but for commercial pur-

poses. At the same time there was this effect, that those who used the method would have to buy the patented apparatus.

Mr. Van Slyke moved to amend the motion by striking out the Cochran and Patrick methods, already published, and inserting a report of the Babcock method, which had but recently appeared.

Mr. Myers moved, as a substitute for the original motion and the amendment, that the reporter on dairy products for the ensuing year be requested to take steps to test the accuracy of the new quick methods for milk analysis and report upon the same. Seconded.

Mr. Voorhees asked whether by the substitute it was proposed to include in the work of the reporter a comparison of the three methods in question with one another or with the gravimetric method. As he understood the substitute the reporter was to study and compare the results of these three methods.

Mr. Myers said that the substitute was so worded as to call simply for tests as to accuracy; the reporter was allowed to use any methods he should choose in testing that accuracy.

Mr. Burney said that inasmuch as certain of the methods under discussion had already been published, it seemed to him eminently proper that the others should appear in the same way, in order that those who cared to test them might have descriptions in convenient form.

Mr. Caldwell said that, as he understood, all the reporters were requested to give a summary of the literature upon their several subjects appearing during the year, and a notice of Babcock's method would therefore be inserted as a matter of bibliography. As to a description of the method, to which most of the members had access, he did not think it worth while to publish that.

Mr. Van Slyke said that an omission to publish a description of the Babcock method would seem unfair to its originator, who was well known to all members of the association as an accurate worker; everything published by him had been of value, and to pass over his method this year, having published methods something like it last year, would seem like ignoring it.

Mr. Wiley said that in Mr. Jenkins's report there was no bibliographical notice of any kind continuing the bibliography of the previous year. If proper, the association might request Mr. Jenkins to furnish a summary of the literature of dairy products from the time of the last report.

The substitute motion made by Mr. Myers was carried.

Mr. Stubbs moved that the reporter on dairy products be requested to furnish a complete bibliography of his subject for the past year. Carried; and the secretary was directed to make the request.

Mr. Penny rose to a point of order. He said that the motion made by Mr. Myers was in the nature of an amendment to substitute one motion for another which was then before the convention; that amendment having been voted upon, the original question was now in order; it had not yet been proposed. As he understood, the original motion

was that the methods which had been discussed should be reported on during the year.

The president said that Mr. Myers's motion had not been understood as an amendment, but as a substitute for the whole question.

Mr. Van Slyke said that a substitute was only one form of an amendment, to be treated like any other amendment.

Mr. Penny said that no member had power to make a substitute; only the association as a body could do that.

The president said that, according to his understanding, the substitute had been carried by the association.

Mr. Penny said that he did not think the association had voted upon the question at issue.

The president asked whether Mr. Penny was in favor of the motion.

Mr. Penny moved to amend the motion by adding the words, *excluding any method, apparatus, or device protected by a patent.*

Mr. Myers accepted the amendment, and the motion was seconded.

Mr. Caldwell said that he should be perfectly willing to exclude patented methods of testing, but he did not think that every piece of patented apparatus should be so excluded; he presumed that the apparatus referred to by Mr. Cooke was patented, and the present motion seemed to require that no method should be tested in which any piece of apparatus used was the subject of a patent.

Mr. Huston said that if care was not taken the power for whirling would be excluded; there were patents on most steam engines.

Mr. Lupton said that reference was now made to certain processes.

Mr. Stubbs said that the motion referred to chemical apparatus.

The president asked Mr. Penny to state the question in full.

Mr. Penny said that the motion was to amend by adding the words *excluding any apparatus or device protected by a patent; i. e.*, excluding from the motion any apparatus or device protected by a patent.

The motion, so amended, was lost.

Mr. Cooke said that the original motion was now in order.

The president said that, as he understood, the original motion had been adopted by the association, and Mr. Penny's motion, which had been lost, was simply a motion to amend the original motion; no further motion was necessary.

Mr. Voorhees asked whether any chemist present had been able to thoroughly extract the fat from the filter paper coils under the Adams method.

Mr. Cooke said that he saw no use in attempting to do so, and therefore never tried it; he took the paper just as it came and made a constant for it. He bought the paper in large quantities and tested individual strips of exactly the same size, cut by machinery. He tested a large number of such strips separately and then together, ascertained the limit of error for the different strips, put the milk directly on the filter paper just as it was received, and then subtracted the constant. The variation between one strip and another was not more than 0.005

of 1 per cent, calculated to 4 per cent milk, and he saw no reason for inserting the requirement that the paper be extracted before use. He moved to amend the method of Adams for determination of fat (page 212) by adding at the end of the first sentence thereof the words *or a constant determined for the paper*. Seconded.

Mr. Farrington said that some work which had been done by a German chemist tended to show that confidence could not be placed in a constant subtraction with ether. The results of his work had been published.

Mr. Wiley said that he had lately had considerable experience in weighing paper of uniform size, and judging by the weights obtained it would seem that paper must vary greatly in thickness; enormous differences might be found in the weight of strips alike in size. It was easy to weigh strips of paper, and he thought that if the amendment proposed should be to get a constant for paper of a given weight and then apply it to the strips, something very accurate would be obtained.

Mr. Cooke said that the variation on 4 per cent milk was very small; the total weight of extract was only about 0.09 of 1 per cent now, and it could vary but very little; if this extract varied one-tenth of its own weight from one paper to another, that would be only 0.01 per cent of fat.

Mr. Wiley said that Mr. Cooke's paper was evidently better than that ordinarily used; Mr. Cook was doubtless familiar with the work upon the subject which had been published in the Analyst.

Mr. Cooke said that he purchased the No. 598 paper.

Mr. Wiley said that the extract matter ought to be very evenly distributed in amount through the paper according to its weight.

Mr. Cooke said that was covered by the wording of the proposed amendment.

The amendment was agreed to.

Mr. Woods said that he had found it more convenient, and he thought more accurate, to run the milk directly from the pipette to the coil than to use the absorption process, and in the case of cream he had found it practically impossible to get a filter paper that would absorb anything like the required quantity. He moved that Mr. Wiley's method be adopted.

Mr. Wiley said that it was a method always used by himself on account of the difficulty stated by Mr. Woods.

The president asked Mr. Wiley to state the amendment.

Mr. Wiley said that it was to run the milk or cream upon the coil directly instead of absorbing it from a beaker, as was originally recommended by Adams, and as the method stood at present. The proposed method was a much better one; a weighed portion of milk could be used without danger of losing a drop if care was taken in running it upon the coil.

The amendment was agreed to; and on motion, the Adams method for determination of fat in milk analysis, as amended, was adopted.

Mr. Myers moved that the alternate method of Morse, Piggot, and Burton for the estimation of fat in milk (page 212) be stricken out. Carried.

Mr. Wiley moved that the alternate method of Babcock for estimating water and fat in milk (page 213) be continued. Seconded.

Mr. Huston said that he had a suggestion to make in regard to the manipulation in the Babcock method; if the air was forced up from the bottom of the tube instead of being drawn down through, the work was much more readily done.

The president asked whether Mr. Huston desired to offer an amendment.

Mr. Huston said that he was uncertain as to the phraseology, but understood that according to the method the air was forced downward.

Mr. Wiley said that the wording of the method did not so require; it only said that the air was to be drawn through.

Mr. Huston said that the method worked well when the air was drawn up, but did not work at all when the air was forced down.

The motion was carried.

Mr. Myers moved that the alternate method of Macfarlane for estimating water and fat (pages 213, 214) be continued. Seconded.

Mr. Caldwell asked whether there was anything particularly valuable in the Macfarlane method; he thought it did not differ much from Babcock's.

Mr. Wiley said that it was a more troublesome method than Babcock's.

Mr. Caldwell said that he saw no necessity for retaining the Macfarlane method, Babcock's being very similar and very good. He moved that the motion made by Mr. Myers be laid on the table. Carried.

Mr. Myers moved that the method for estimation of sugar in milk (pages 214, 215) be continued. Carried.

Mr. Wiley moved that the method of reduction of sugar by alkaline copper solution be added as an alternate method. Carried.

Mr. Myers moved that the method for estimation of ash in milk (page 215) be continued. Seconded.

Mr. Woods moved to amend the method by striking out the words "in muffle." He said that he saw no necessity for specifying in what the substance should be charred, it being specified that it was to be burned at a low red heat.

Mr. Wiley said that for the sake of safety he thought it better to incinerate in a muffle, but it could be done without.

Mr. Myers accepted the amendment, and the motion, as amended, was carried.

Mr. Myers moved that the methods for analyses of butter and milk, as amended, be adopted. Carried.

On motion, the convention adjourned until Friday morning at 9.30 o'clock.

SECOND DAY.

MORNING SESSION, FRIDAY.

The convention was called to order by the president at 9:30 o'clock.

The president appointed, as a committee to consider and report upon the recommendations contained in his opening address, Messrs. Myers, Wiley, and Kedzie.

Dr. Lupton presented the following report:

REPORT ON POTASH.

By N. T. Lupton.

Since the last meeting of the Association, nothing whatever of interest on the determination of potash has been published, so far as my reading and observation have extended.

The methods recommended by this Association seem to give general satisfaction, and no suggestions of change or improvement have been made by those with whom your reporter has been in correspondence. Some points of interest in reference to the determination of moisture and the destruction of organic matter have been under investigation, but the results are not sufficiently advanced to be embodied in this report.

Samples, as usual, were prepared and sent to different chemists connected with experiment station work with a request to observe the following points:

(1) Determine moisture and potash strictly according to official methods and report the method or methods used.

(2) Make such suggestions of improvement in present methods as may be justified by experimental results, and report the results in detail.

The samples were obtained from manufacturers and dealers, and represent commercial goods, such as are in common use by farmers and planters. They were selected with reference to the difficulties usually met with in station work in the determination of potash, and as well suited to test the accuracy of our methods.

Four samples were sent, as follows:

(1) Commercial kainite.

(2) Cotton-seed meal.

(3) A commercial fertilizer, labeled, "Bone and potash."

(4) A commercial fertilizer, labeled "High grade vegetable fertilizer."

The manufacturer of "Bone and potash" says: "The formula is bone phosphate, rock, sulphuric acid, and muriate of potash. These are the only ingredients used." The manufacturer of the "High grade vegetable fertilizer" says: "The ingredients from which we derive phosphoric acid are mainly ground animal bone, but there is a small portion of high grade phosphate rock and also 38 per cent available phosphate and tankage. The sources of ammonia are the ground bone, tankage, dried blood, sulphate of ammonia, and a small portion of cotton-seed meal used as a drier. The source of potash is muriate of potash and the potash that may be in the small quantity of meal above mentioned."

The results reported from twelve agricultural experiment stations by seventeen chemists, making thirty-two determinations of potash in each sample, are presented in a tabular form as follows:

Station and chemist.	1. Kainite.		2. Cotton-seed meal.		3. Bone and potash.		4. High grade vegetable fertilizer.	
	Moisture.	Potash.	Moisture.	Potash.	Moisture.	Potash.	Moisture.	Potash.
1. Connecticut: Messrs. Winton & Curtis	9.80	11.78 11.84	6.25	1.86 1.89	18.40	3.82 3.93	9.53	3.64 3.71
		11.81		1.87½		3.87½		3.67½
2. Massachusetts: W. H. Beal	9.68	11.50 11.53	6.91	2.13 2.16	18.69	4.02 4.01	9.87	3.87 3.88
		11.51½		2.14½		4.01½		3.87½
3. New Jersey:								
E. B. Voorhees	8.69	12.00	7.69	1.50	17.96	3.94	9.32	3.88
L. A. Voorhees	.....	12.00	.....	1.66	.....	3.90	.....	3.89
C. G. Cathcart	.....	12.04	.....	1.63	.....	4.01	.....	3.90
		12.01		1.60		3.95		3.89
4. Pennsylvania: W. S. Sweetser	11.70 11.75	12.08 12.06 11.83 11.93	.....	1.74 1.74 1.71 2.04 2.13 2.17	17.81 17.83	4.21 4.16 4.18 4.20 4.18	8.85 8.95	3.91 3.95 3.97 3.96 4.19 4.21
	11.72½	11.97½		1.92	17.82	4.18⅝	8.90	4.03
5. Maryland: H. J. Patterson	8.67	12.78	6.45	1.56 2.11	18.46	4.33	9.61	4.21 4.23
				1.83½				4.22
								(3.28 2.42)
6. Illinois: E. H. Farrington	9.80	12.33	8.15	1.31	20.37	4.28	11.40	4.01
7. Kentucky: H. E. Curtis	9.07	11.76	6.44	1.55	18.03	4.09	9.60	3.90
8. West Virginia: H. R. Baldwin, jr	.....	11.63	.....	1.71	.....	4.10	.....	3.91
9. North Carolina:								
J. R. Harris	9.19	11.44 11.36 11.44	5.92	1.47 1.49	17.68	4.15 4.15	14.51	4.06 3.94 3.92
B. W. Kilgore	.....	11.30 11.16 11.16	.....	1.67 1.84 1.88	.....	4.23 4.23 4.24	.....	4.06 4.05 4.09
		11.31		1.67		4.20		4.02
10. Louisiana: B. B. Ross	10.01	12.12 12.02	6.15	a2.20 a2.21 b1.99 b2.05	17.87	4.00	8.99	3.83 3.82
		12.06						3.82½
11. U. S. Department of Agriculture: Aug. E. Knorr	6.92 7.01	11.59 11.42 11.66 11.50	6.57 6.45	1.85 1.75 1.69 1.73	19.29 19.50	3.92 4.11 4.27 4.14	9.98 10.05	3.97 3.94 4.19 4.19
	6.97	11.54	6.51	1.75½	19.40	4.11	10.02	4.07
12. Alabama: I. T. Anderson	9.45	11.87	5.81	1.94	20.85	3.93	.....	.....
P. L. Hutchinson	9.02	11.65 11.68 11.71 11.71	6.59	2.00 1.94	20.72	4.15 4.17	9.29	3.91 4.02
	9.23	11.72	6.20	1.96	20.78	4.08		3.96

Notes on the above received from those taking part in the work:

1. *Connecticut.*—The platinum solution gave theoretical results with pure salt. I should hardly expect any close agreement by different chemists on the sample of kainite; it seemed to me altogether too coarse. In reference to moisture, which was determined about a month after potash, the analyst says, under date of July 8: "As these samples have stood in partly filled bottles since June 28, when the potash determinations were made, I do not imagine that these water determinations represent accurately the quantity of water contained in the samples as received."

3. *New Jersey.*—With the exception of sample No. 2, the Lindo-Gladding method was used. The 1.50 per cent was secured by igniting the sample at low red heat and extracting potash with boiling water. In the other cases the alternate method of the Association was used in making the solution. Moisture in No. 2 was determined by drying in hydrogen. In all other cases the methods prescribed by the Association were used. We have nothing to suggest in the way of improvements on present methods.

4. *Pennsylvania.*—Determinations were made by three methods: (1) The water-soluble by the Lindo-Gladding method. (2) Water soluble by the alternate method. (3) Total soluble in nitric acid and a few drops of hydrochloric acid by the Lindo-Gladding method. The results on the total were very variable, and always too low when sulphuric acid was used to destroy the organic matter of Nos. 2 and 4, and the residue was burned to whiteness.

5. *Maryland.*—The Lindo-Gladding method was used. The low result in No. 4—3.28 potash—was evidently caused by the volatilization of some of the potash even with the utmost care. The incineration was done before boiling. The low result in No. 4—2.42 potash—is no doubt due to being held by the calcium sulphate which is formed in a hard mass. In this case the organic matter was destroyed with sulphuric acid.

7. *Kentucky.*—The official method, modified by Gladding, was used. In determining moisture, No. 1 was dried at 130° C. until the weight was constant. Nos. 2 and 4 were dried at 100° C. for five hours.

8. *West Virginia.*—The analyses were made by the method of Lindo as modified by Gladding. Nos. 1 and 2, averages of three determinations each. Nos. 3 and 4, averages of two determinations each.

9. *North Carolina.*—Washing with Gladding solution in dish gave better results than washing after transfer to crucible.

10. *Louisiana.*—In securing the results reported as *a* the sample of cotton-seed meal was saturated with sulphuric acid, heated for several hours until an ash, moderately gray in appearance, was obtained. It was then moistened with a few more drops of sulphuric acid, heated gently at first and then strongly over the blast lamps until all traces of carbon were destroyed and a transparent, vitreous mass was obtained. It was then dissolved in hot water, with the addition of a few drops of HCl and potash was determined in the usual manner. The results marked *b* were reached by simply igniting sample without previous moistening with sulphuric acid.

11. *U. S. Agricultural Department.*—The methods of analysis were strictly according to those adopted by the Official Association in the meeting of 1889.

The following table presents the results of each station reduced to the same percentage of moisture, viz: No. 1, 9 per cent; No. 2, 6.50 per cent; No. 3, 18.50 per cent; No. 4, 9.50 per cent. The table also presents the variation of each from the general averages:

Station.	Potash with 9 per cent. moisture.	Variation from average.	Potash with 6.50 per cent moisture.	Variation from average.	Potash with 18 50 per cent. moisture.	Variation from average.	Potash with 9.50 per cent. moisture.	Variation from average.
1 Connecticut.....	11.91	—0.01	1.87	+0.08	3.85	—0.26	3.67½	—0.29
2 Ma sachusetts..	11.60	—0.32	2.15	+0.36	4.02	—0.09	3.89	—0.08
3 New Jersey.....	11.97	+0.05	1.62	—0.17	3.92	—0.19	3.88	—0.09
4 Pennsylvania...	12.34	+0.42	1.92	+0.13	4.15	+0.04	4.00	+0.03
5 Maryland.....	12.73	+0.81	1.82	+0.03	4.33	+0.22	4.22	+0.25
6 Illinois.....	12.44	+0.52	1.33	—0.46	4.38	+0.27	4.10	+0.13
7 Kentucky.....	11.77	—0.15	1.55	—0.24	4.07	—0.04	3.90	—0.07
8 West Virginia..	11.63	—0.29	1.71	—0.08	4.10	—0.01	3.91	—0.06
9 North Carolina	11.33	—0.59	1.66	—0.13	4.15	+0.04	4.25	+0.28
10 Louisiana.....	12.19	+0.27	2.10	+0.31	3.97	—0.14	3.80	—0.17
11 U. S. Dep. of Ag.	11.29	—0.63	1.75	—0.04	4.16	+0.05	4.09	+0.12
12 Alabama.....	11.75	—0.17	1.95	+0.16	4.19	+0.08	3.96	—0.01
Average.....	11.92	.....	1.79	.....	4.11	.....	3.97	.....

These results, with two or three exceptions, are in close accord, and show that with proper care in manipulation and in the preparation of reagents employed, reliance can be placed on the results obtained by our methods.

The extension and rapidly increasing use of fertilizers has brought the skill of the agricultural chemist into greater demand than ever before, while the vast pecuniary interests involved have imposed additional obligations upon the analyst to spare no pains to secure the greatest possible accuracy. Of course, in the execution of commercial work, he should not be unmindful of his obligation to contribute as much as possible to the progress of pure science along whatever lines may be suggested by his daily work.

A continuance of the present methods of determining potash is recommended for the ensuing year. There are some slight changes in the directions given for carrying out the official methods which your reporter believes would be improvements.

(1) As recomended and adopted last year, it should be clearly stated that the precaution of charring organic substances, like cotton-seed meal, etc., and incineration with the addition of strong sulphuric acid must be observed with the Lindo-Gladding as well as with the alternate method.

(2) After boiling 10 grams of the fertilizer with 300 cubic centimeters of water for thirty minutes, as stated in the Lindo-Gladding method, add ammonium oxalate and ammonia before instead of after cooling. In other words, strike out "cool the solution."

(3) In the case of ordinary fertilizers there seems to be a waste of platinum solution by using 10 cubic centimeters containing 1 gram of platinum. From one-third to one-half this amount gives accurate results. One gram of the solution mentioned is theoretically capable of precipitating 0.4782 gram of potash, equivalent to 47.82 per cent.

(4) In the directions for carrying out the alternate method there is ambiguity in the statement about pulverizing. It reads as though the fertilizer is to be charred and ignited before pulverization.

The president introduced Hon. Edwin Willits, Assistant Secretary of Agriculture, who spoke as follows:

ADDRESS OF HON. EDWIN WILLITS.

Mr. President and gentlemen of the Association of Official Agricultural Chemists: I am gratified to see you this morning, having awaited with a good deal of interest the time for your assembling again in convention after testing some of the formulas which you elaborated last year and the year before. The very paper to which we have just

listened clearly indicates that you are greatly interested in your work and in the results you bring about by using, as you suppose, exactly the same methods. The personal factor enters into a chemical analysis as well as into all the affairs of life; the manipulation, the individuality, can be found there as well as elsewhere. Now, how can you average unless you compare these results, and how can what may be considered a false tendency be eliminated otherwise than by comparison?

The subject of chemistry is very deep and intricate; it is almost as old as the human race, and before it there is a great future. We have the consoling thought that in no line of investigation has all knowledge yet been attained. It does seem as though we are just on the eve of wonderful discoveries in your field and in others, and as I sit at my desk receiving the reports as they come in from all over this country, and mindful of the fact that nearly five hundred intelligent, scientific men are investigating the secrets of nature, my heart fairly bounds in contemplation of what may be the results of their work; and yet the consoling thought remains that though we may discover great things to-day or to-morrow, there is still a fountain of mystery, a wealth of intelligence, a wonderful source of law established by the Creator throughout all nature, and which the human mind may study for all ages and never compass. Great discoveries have been made heretofore, and looking back upon the acts of the great chemists you will sometimes wonder, What can we do? Can we find anything new? Can we accomplish anything? But it is certainly true that there are secrets yet to be divulged, and it may even be that one of these small keys that you yourselves are handling in the study of one of these seemingly small questions shall serve to unlock the depository of vast stores of knowledge, human and divine.

I believe in the experiment stations, and my hearty sympathy is with them; but my sympathy is most heartily with the chemists, because the experiment station was born in the chemical laboratory, of which it is an evolution; and probably so long as experiment stations shall exist the results obtained by all their other investigators shall be weighed and tested in the laboratories of their chemists. For there is something strange about this chemistry. Just as all the laws of nature are to be reduced to mathematics, so these investigations all center in the chemist's laboratory; and whatever of instruction you may get, whatever of information you may gather, and whatever new light may be thrown upon your work, I can most heartily understand and appreciate that your gain shall redound to the benefit of scientific investigators in all directions. The application of formulas will make results more certain. Of course mistakes have been made in the past and are being made now, and it is the correction of mistakes and errors that shall lead to more definite and final results.

I trust that your meeting this year may be successful, and that your work during the following year may be more nearly perfect and

complete; that your investigations and experiments may be conducted along more accurate lines, so that we may rely upon what you shall send to us as the proper analyses, not only of fertilizers, but of all the other matters which you are called upon to determine. I hope that you shall go back to your laboratories with renewed strength and with improved knowledge and information. I thank you for your kindness in asking me to show my sympathy—and I can do no more this morning—by appearing before you and encouraging you in your work.

The president stated that discussion upon the subject of potash was now in order.

Mr. Dancy said that there seemed to be a mistake in the phraseology of the Lindo-Gladding method (page 223), which had probably escaped the attention of the association, having been allowed to stand as it was for two or three years; he referred to the addition of the oxalate before the hydrate of ammonia. He would suggest that the ammonium hydrate be added before the ammonium oxalate; *i. e.*, that the solution be first made alkaline with ammonia, and the oxalate be added thereafter.

Mr. Gaines asked what difference that would make.

Mr. Dancy said that when the oxalate was added before the solution was made alkaline the lime present in combination with phosphoric acid was immediately precipitated. After the phosphate of lime was precipitated by the ammonia the oxalate was added to combine with whatever lime might be left in the form of sulphate. The oxalate, if added first, was used up in precipitating, as far as it went, from the general lime content. He saw no very good reason for adding the ammonia in slight excess, believing that a safe excess of ammonia would secure better precipitation.

Mr. Huston said, in regard to the last step in the operation, that of weighing the double salt of platinum, he had used a method which differed slightly from the manipulation prescribed, and which was suggested to the association some years ago, being that of filtering on an ordinary paper filter and dissolving the double salt with hot water after thorough washing. He had never failed to find on the filter papers, even in the Lindo method, a very appreciable residue of a material which was not double salt of platinum. He had therefore stopped using the Gooch crucible, and found it satisfactory to evaporate in a platinum dish. He thought it possible that some of the differences in results arose from something other than double salt which went into the crucible, but this was to be taken as a mere suggestion.

Mr. Frear said that in making a large number of duplicate determinations he had in one set left out the salt solution, and was curious to see what difference that would make in the ordinary run of commercial fertilizers. 0.0436 of 1 per cent was the mean difference, and the differences greater than 0.1 of 1 per cent were only two out of fifty; the

differences greater than 0.05 of 1 per cent where the salt was used and where it was not occurred in seventeen cases out of fifty. He had been able to work with equally good results without the salt solution in the case of ordinary fertilizers, and the method was a good deal more rapid. He simply desired to state the fact and to hear what there was to be said upon the other side.

Mr. Dancy said, again referring to the matter of the oxalate, that he wrote last year to Mr. Jenkins, who was then the reporter on potash, calling his attention to the order in which the two reagents were added. Mr. Jenkins had replied that the fact had theretofore escaped his notice, and that it was probably a mistake which had been overlooked from time to time; that he himself had never added the reagents in the order prescribed by the method as worded. The speaker would move that the ammonia be added first, and then the oxalate, and that the word "slight" be omitted.

Mr. Kedzie suggested that the words "cool the solution" be stricken out.

The president asked Mr. Dancy to state the proposed amendment specifically.

Mr. Dancy said that the amendment would so alter the method as to make it read as follows:

> Boil 10 grams of the fertilizer with 300 cubic centimeters of water for thirty minutes. To the hot solution add ammonia in excess and then a little ammonium oxalate, thus precipitating all phosphate and sulphate of lime, oxide of iron, and alumina, etc.; make up to 500 cubic centimeters, etc.

the remainder of the paragraph being allowed to remain as at present.

Mr. Lupton asked whether it was intended to strike out the words "cool the solution."

Mr. Dancy said that his amendment included the striking out of those words before the direction to add the ammonia.

Mr. Kedzie said that as Mr. Dancy, being a commercial chemist, was not in a position to make the motion in question, he (Mr. Kedzie) would make it in his own behalf. He moved to strike out the words, "cool the solution; add a little oxalate of ammonia and then ammonia in slight excess," and to insert in the place thereof the words, "to the hot solution add ammonia in excess and then a little oxalate of ammonia."

Mr. McDonnell asked why it would not be well to strike out "cool the solution," and not to say, "to the hot solution add," etc. Then either the hot or the cool solution could be chosen.

Mr. Kedzie said that he thought better results were obtained by adding to the hot solution directly.

Mr. Voorhees said that he could see nothing to be gained by striking out the words "cool the solution." The chemists were obliged to cool the solution before filling to the mark, and it seemed to him better to make the additions to the cool solution. He asked what advantage would be gained by making the proposed change.

Mr. Dancy said that it had been his idea that the precipitation was more complete in the hot solution.

Mr. Myers said that if the solution were boiling it would, of course, drive off the ammonia; but the method only said "hot," and the precipitation would take place better in a moderately hot solution than in a cold one; it was of advantage to have the solution hot, but not boiling.

The amendment as proposed by Mr. Kedzie was carried.

The president said that he understood the amendment as covering the recommendation of the reporter (Mr. Lupton).

Mr. Lupton said that it did.

Mr. Robinson said that he should be glad to hear the experience of chemists in regard to the recommendation suggested last year, he believed by Mr. Jenkins, in regard to the use of one filtration instead of two (page 224). It was recommended by Mr. Jenkins that but one filtration be made; in other words, that the oxalic acid and ammonium oxalates be added immediately before the filtration, and that one filtration would suffice. His own experience was that this would very much facilitate the work, and without any sacrifice of accuracy.

Mr. Frear said that last year he had quoted the experience of the Maine station, where the method referred to was used exclusively. The chemists there said that in using this method they found no difference in their results over the theoretical result; that their results were concordant whether they used two filtrations or one, and that when both reagents were used at the same time the filtrations were much more rapid.

Mr. McDonnell said that the method in question was presented by Mr. Bartlett, of the Pennsylvania State College, some years ago, he having made a number of perfectly satisfactory experiments with it. Mr. Bartlett had since used it at the Maine station, where also it had given satisfaction. In the speaker's own experience it had proved better to filter all the precipitates together than to separate them.

Mr. Huston said that he was much surprised to hear Mr. Jenkins quoted as in favor of the method under discussion, for he remembered a conversation which took place about four years ago between Messrs. Richardson and Jenkins, in which the latter took the other side and objected very seriously to having the oxalate added before the barium hydrates were filtered off.

Mr. Frear asked whether Mr. Jenkins's objection was made as a result of experience or simply on theory.

Mr. Huston said that he did not know upon what Mr. Jenkins had founded his statement, but he had made a very positive one. He could not recollect just what Mr. Jenkins had said, as it was some years ago.

Mr. Van Slyke said that there seemed to be no definite data at hand in regard to the subject; he would therefore move that the reporter be requested to ask the analysts at the time of sending out the sam-

ples to make comparative determinations by one and two filtrations. This would give the association some definite data, and would place it in a position to act intelligently upon the question next year.

Mr. Cooke said that comparatively few chemists used the single filtration method at present, and it would be very difficult to get men to double or treble their work on the samples in testing a method not used in their laboratories; the Lindo-Gladding method was used in almost all the stations.

The motion was carried.

Mr. Myers said that the reporter had very properly called the attention of the association to an ambiguity or repetition to be found under the head of "Alternate method," at the foot of page 223 and top of page 224; the description was partially doubled. He moved that such ambiguity be removed by rearranging the first two sentences under the head of "Alternate method" so as to read as follows:

Pulverize the fertilizer (200 or 300 grams) in a mortar; take 10 grams. In case the potash is contained in organic compounds like tobacco stems, cotton-seed hulls, etc., it is to be saturated with strong sulphuric acid and ignited in a muffle to destroy organic matter.

Then proceed as prescribed—"Boil for ten minutes," etc.

Mr. Woods said that in some States the law prescribed the determination of potash soluble in water.

The president said that the association could not help that.

The motion was carried.

Mr. Huston said that he was compelled to work under such a law as Mr. Woods had referred to; the Indiana law said "potash soluble in water;" it did not say how long the treatment in water was to be continued, or whether the water was to be hot or cold. He had a certain class of goods which gave 0.7 in water and double that amount after treatment with sulphuric acid; he would like to have an expression as to the availability, at least, of that potash. Formerly he had ignited the goods, but a strict interpretation of the law would not allow that to be done, and as a result a good deal of fault was found with his work. He believed that potash which did not dissolve readily in water was none the less available for fertilizer purposes, but of course it could not be said to be soluble in water.

Mr. Myers said that his attention had recently been called by Mr. Jenkins to the fact that much of the chloride of platinum now on the market was adulterated with chloride of iron, and it was hard to get it purified. This was an unexpected and rather serious adulteration, and chemists should look out for it.

The reporter had called attention to some changes with reference to charring; he would like to hear the recommendation read.

Mr. Cooke said that if it was allowable he would move to take up all of Mr. Lupton's recommendations.

The president said that only one had been made, and that had been

passed upon; the matter referred to was probably in the nature of a suggestion.

Mr. Lupton said that in the alternate method the directions in regard to pulverizing, being ambiguous, had been changed. If permitted, he would read the slight changes proposed in his report. The first was as follows:

(1) As recommended and adopted last year, it should be clearly stated that the precaution of charring organic substances like cotton-seed meal, etc., and incineration, with the addition of strong sulphuric acid, must be observed with the Lindo-Gladding as well as with the alternate method.

That was adopted last year, but was not incorporated in the directions. Southern chemists had cotton-seed meal in all or nearly all of their complete fertilizers, and the charring was necessary. An interesting article on "Potash in Soil and Plants," by Berthelot and André, was published in Comptes Rendus, 105, pages 833 and 911, and an abstract of the same appeared in the Journal of Analytical Chemistry, Vol. II, 1888, pages 221 and 223. Presuming that nearly all the members of the association had seen this, he had not included it in his report. The article contained the following statement:

The potash in a plant may be divided into three parts:
(1) That which is easily soluble in water.
(2) That difficultly soluble in water and soluble in dilute acids.
(3) That retained by the tissues of the plant against the solvent action of water and dilute acids.

This showed the importance of charring with a strong acid, such as sulphuric acid, in order to get out all the organic substance.

The president said that as he understood Mr. Lupton's recommendation it was that the clause directing the charring should be inserted also in the method of Lindo as modified by Gladding.

Mr. Lupton said that the president's understanding was correct; the recommendation was really adopted last year, but had not been inserted.

Mr. Kedzie asked what was to be done in States where the water-soluble was required by law.

The president said that in those States the law would have to be followed; the recommendation was applicable to States which had no such law.

Mr. McDonnell asked whether it would not be necessary for a manufacturer who sold his goods in two States, one of which had such a law and the other of which had not, to make different analyses and give different guaranties.

The president said that it would.

Mr. Lupton said that in the report of last year Mr. Jenkins had said (page 82, top):

It has been abundantly proved in past years that it is necessary to char such vegetable products as cotton-seed meal previous to extraction in order to accurately determine either the potash or the phosphoric acid, and I therefore feel justified in taking the higher figure, 1.90 per cent, as correct.

Mr. Battle said that he was in favor of the amendment indicated, but would like to inquire to what extent it could be known whether cotton-seed meal was present in the fertilizer. If the fertilizer was ammoniated entirely with cotton-seed meal there would be no trouble in distinguishing the fact, but a small amount of cotton-seed meal in the fertilizer could not be distinguished from the color; how then, in such a case, could it be known that it was necessary to char? The same trouble also existed in regard to tobacco stems. In North Carolina the potash in two or three brands was from tobacco stems, and in some cases it could not be told from the appearance how much or whether any stem was present, and it was therefore difficult to know whether to char or not.

Mr. Lupton said that the direction was to char in the case mentioned. It said:

In case the potash is contained in organic compounds like tobacco stems, etc.

Mr. Battle said that what he wished to know was how it could be determined whether or not the material was present in the fertilizer.

Mr. Huston said that he had fair success in detecting the material by noticing its behavior when wet; he thought that he could always tell when he had the soluble phosphoric acid leached out; he would not say that he could tell positively in that way, but it was very helpful in determining whether organic compounds were present.

The amendment was agreed to.

Mr. Lupton said that the next suggestion had been passed upon; the words "cool the solution" had been stricken out, and it had been directed that ammonia in excess and then oxalate of ammonia should be added to the hot solution. The next suggestion was as follows:

In the case of ordinary fertilizers, there seems to be a waste of platinum solution by using 10 cubic centimeters, containing 1 gram of platinum. From one-third to one-half this amount gives accurate results. One gram of the solution mentioned is theoretically capable of precipitating 0.4782 gram of potash, equivalent to 47.82 per cent.

In the alternate method (page 224) the amount of platinic chloride directed to be used was 10 grams, which was excessive, as accurate results could be obtained with less. He merely wished to call attention to the fact.

The president said that no amendment was proposed; it was only suggested that smaller quantities be used. He supposed that no more was required than was sufficient to precipitate the potash and other salts present.

Mr. Huston said that the platinum solutions in the two methods were not alike.

It was moved that the methods for determining potash, as amended, be adopted. Carried

Mr. Caldwell presented the following report:

REPORT ON THE ANALYSIS OF CATTLE FOODS.

By G. C. Caldwell.

This report is presented in three parts. In Part I an abstract is given of the journal literature on the subject from August, 1889, to August, 1890. Part II consists of the results of the analyses of the three samples sent out by the reporter, together with comments on the work, and supplementary investigations made by the analysts themselves. In Part III the reporter's recommendations for the ensuing year are offered.

PART I.

AN ABSTRACT OF THE JOURNAL LITERATURE ON THE SUBJECT.

THE HYDROSCOPIC WATER.

P. Baessler. Ueber die Bestimmung des Fettgehaltes der Mohnkuchen. Die Versuchs-Stationen, XXXVI, 367.

The author finds, in some experiments with poppy-seed cake, that the determination of moisture gives lower results if the drying is done in air than if done in a current of hydrogen.

The Connecticut Agricultural Experiment Station. Apparatus for drying in hydrogen, by W. L. Winton. Annual report for 1889. Journal Analytical Chemistry, IV, 175.

——— Drying oven. Annual report, 1889, 195. Journal of Analytical Chemistry, IV, 184.

Very large, to take in long pieces of fodder, as cornstalks.

——— Hydrogen generator, by S. W. Johnson and T. B. Osborne. Annual report, 1889, 181. Journal Analytical Chemistry, IV, 169.

THE ASH.

W. Kwasnik. Das Calciumplumbat und seine Verwerthung zur Aschenbestimmung von vegetabilischen Substanzen, etc. Berichte der Deutschen Chemischen Gesellschaft, XXIII, 1890. Abstracts, 363.

A series of experiments has shown that the incineration is much sooner completed if one adds a weighed quantity of calcium plumbate. This salt gives a part of its oxygen to the combustible substance, and it is easily regenerated by taking up more oxygen from the atmosphere.

H. J. Patterson. Investigation on the determination of moisture in air-dry feeding stuffs. Annual Report Maryland Agricultural Experiment Station, 1889.

Over two thousand determinations made in the course of the study of the subject with reference to the questions—in what kind of a vessel to dry, how long to dry, at what temperature, in what medium, and what is the nature of the substance lost, and the general change in the process of drying. Slightly higher average results were obtained on drying in crucibles as compared with watch glasses. Generally the amount of loss increases with elevation of temperature and greater length of time of drying. No special and universal advantage was found in the use of any one medium over another in which to dry the substance. At the close of this report of progress the author states that "there can be no doubt that temperatures above 100° C. and heating for a longer time than six hours are to be used with great caution."

G. H. Failyer and J. T. Willard. Methods of analysis of feeding stuffs. The water. Annual Report Kansas Agricultural Experiment Station, 1889, 117.

Apparatus described to facilitate the desiccation in hydrogen. The authors conclude that complete drying is not assured in less than twenty to thirty hours. Figures are given in support of this conclusion.

P. Baessler. Ueber die Bestimmung des Fettgehaltes der Mohnkuchen. Die Versuchs-Stationen, XXXVI, 367.

The author refers to his having already shown that in the case of linseed cake the results of the determination of the ether extract are too low if the substance is first dried at 100°, unless in a current of hydrogen. He finds that the same is true with reference to poppy-seed cake. The result is also too low if the substance is dried in a vacuum over sulphuric acid.

He found that a small quantity of an apparently oily substance was carried over into the absorption apparatus by the current of hydrogen. But since the results of the ether extract determination on the substance dried in hydrogen are concordant, and higher than if made on substance dried in any other way, he concludes that this is not real fatty substance.

He proves that oxygen is absorbed when the substance is dried in air and carbon dioxide is given off.

If the substance is not heated above 90° in air it is almost fully dried in three hours, and a determination of ether extract on the substance so dried gives the same result as on the substance dried in hydrogen. It can not be heated higher than this without loss of fat, while linseed cake can be heated to 95°.

E. Wrampelmeyer. Die Bestimmung des Leinkuchenfettes. Die Versuchs-Stationen, XXXVI, 1889, 287.

Mentioning the papers by Baessler, Klopsch (Fresenius Zeitschrift für analytische Chemie, XXVII, 1888, 452), Märcher, Soxhlet, Stutzer, Bühring, and Siewert, and the want of full agreement between the results and conclusions of these authors, the author makes determinations covering some of the points in dispute, and proposes the following method:

For the extracting agent the ether need not be wholly dehydrated; shaking up the commercial article with calcium chloride is sufficient.

The air-dried substance is to be dried for one hour at the temperature of boiling water in a current of illuminating gas.

The extraction is to be made in a syphon apparatus, for three hours, and the rapidity of the boiling of the ether is to be so regulated that from one to one and one-half minutes elapses between the syphonings.

The residue left after distilling off the ether is to be dried for one hour at 95° to 98° in a Meyer drying oven.

R. S. Curtiss. Comparison of solvents for fat in feeding stuffs. Annual report of Connecticut Agricultural Experiment Station for 1889, 250.

Ether, gasoline boiling at 45° to 50°, petroleum benzine boiling at 55° to 60°, petroleum benzine boiling at 75° to 80°, and chloroform were compared. The petroleum benzine was the most unsatisfactory of all; that and chloroform dissolve quite as much chlorophyll as ether does. No proof is found that the extract by benzine represents true fat more nearly than the ether extract does.

P. H. Irish. An apparatus for use in the determination of fat in plant substance. Bulletin No. 4, Oregon Agricultural Experiment Station, January, 1890.

For distilling from the extract and drying and cooling the fat in an atmosphere of hydrogen.

H. J. Patterson. The use of animal charcoal in the determination of fat in fodders. American Chemical Journal, XII, 1890, 261.

Puts in the percolation tube first animal charcoal, on that a plug of cotton, then the substance to be extracted, then another plug of cotton. The author proved that there was no loss of fat in the passage of the ether extract through the charcoal, the results being the same, in tests with pure fat, with and without the charcoal; on feeding stuffs the results were always higher without than with the charcoal, and with some kinds of fodder the differences were very large. The product obtained with

the charcoal is nearly pure fat; the charcoal takes up any water that may accompany the fat, and also ether-soluble acids from the plant substance, or formed from the ether as the result of the continuous distillation; the result of the ether extract determination is not so much affected by the age of the sample as without the use of charcoal.

G. C. Caldwell. An apparatus for the drying of substances in hydrogen. Bulletin XII, 1889, Cornell University Experiment Station.

THE FIBER.

G. Lange. Die Bestimmung der Cellulose. Zeitschrift für physiologische Chemie, XIV, 1889, 282.

By fusion of the substance with caustic alkali the author separates cellulose from Lignin; he seems to propose this as a method for the determination of fiber.

Cross and Bevan. The estimation of cellulose. Chemical News, LXI, 1890, 87.

G. H. Failyer and J. T. Willard. Methods of analysis of feeding stuffs: the crude fiber. Report of Kansas Agricultural Experiment Station, 1889, 119.

Connects the flask during the boiling with an inverted condenser, and also conducts in a blast of air which impinges on the surface of the liquid and keeps the foaming of the liquid under control.

G. Heinzelmann. Bestimmung der Holzfaser in Weizenkleie. Zeitschrift für angewandte Chemie, 1889, 557.

(See under Nitrogen-free extract.)

W. A. Withers. Some points on the determination of fiber in feeding stuffs. Journal of Analytical Chemistry, IV, 1890, 36.

The author gets more rapid filtration by treating the substance with NaOH first; the results that he obtains are concordant with those obtained by the usual method. He recommends covering the asbestos welt with glass wool for more rapid filtration, and conducting a current of air against the surface of the liquid while boiling with the reagents to prevent frothing. From his tests of the use of acid and alkaline solutions of different degrees of strength, and of treatment for different periods of time, he concludes that differences in the results follow such variations.

M. Honig. Zur Bestimmung der Rohfaser und der Stärke. Chemisches Centralblatt 1890, 2, 275.

The substance is heated to 210° with glycerine; the cooled mass is poured into alcohol (95 per cent), ether is added, the precipitate is filtered, and washed with a mixture of alcohol and ether (5 to 1), dried on a porous plate, treated with hot water then hydrochloric acid is added, and the mixture is heated half an hour under a return flow condenser, and filtered; the cellulose is on the filter, the starch in the solution. Analyses are given, showing good results.

THE NITROGEN-FREE EXTRACT.

G. Heinzelmann. Bestimmung der Stärke in Weizenkleie. Zeitzchrift für angewandte Chemie, 1889, 557.

The determination of fiber and starch in bran by the ordinary methods is inaccurate, the former being too low and the latter too high. He compared the determination of starch by treatment with .05 per cent lactic acid for two and a half hours under pressure of 3.5 atmospheres, and by treatment with malt extract; by the former method results were too high. The latter is the only reliable method.

IN GENERAL.

Fodder: Methods of analysis agreed upon at the International Chemical Congress at Paris. Chemisches Centralblatt, 1889, 2, 938.

Connecticut Agricultural Experiment Station. Grinding fodder; use of Otto gas engine. Annual Report 1889, 202.

PART II.

THE RESULTS OF THE ANALYTICAL WORK.

A copy of the official method was sent early in the fall of 1889 to each experiment station, with an invitation to coöperate in this work if the facilities were possessed for carrying out the method in all its details. Many of the stations accepted the invitation. Twenty reports have been received, including two distinct ones from the Pennsylvania Station.

The official method was followed apparently everywhere in all its essential details; in respect to such unimportant matters as the kind of filter used in the determination of the fiber, or the use of a blast of air to check the foaming in the same determination, or the mode of standardizing the acid and alkaline solutions in the determination of nitrogen, methods were followed in a few cases that differed from those officially prescribed. Only one important departure was noticed, the use of 5 per cent acid and alkali in the determination of the fiber in the laboratory of the Department of Agriculture.

Three samples were sent to each analyst, hay, wheat middlings, and linseed meal. The hay was first cut as fine as practicable in an ordinary hay cutter and a thoroughly mixed sample of this was ground in a steel mill, sifted through a sieve of the prescribed size of mesh; that which would not pass through was ground again and sifted, and this operation was repeated till the whole was reduced to the required degree of fineness. The whole of the powder thus obtained was then carefully mixed on a large sheet of paper. The middlings and linseed meal were ground, sifted, and mixed in the same manner.

The results of the analyses, calculated to dry substance by each analyst, are given in the following tables, and the extent of divergence in the results is exhibited in the same manner as it was in my report on the work of the preceding year. In making these calculations, in a very few instances the widest differences from the average were not included, when the divergence from the results obtained by all the other analysts was so great as to justify such omission. [More of these widely divergent results were omitted in the final preparation of this report for the press. This will explain the differences between the results of the calculations presented at the meeting, and those which are given here.—G. C. C.]

HAY.

State.	Analyst.	Moisture.	In the dry substance.						
			Pure ash.	Ether-extract.	Crude protein.	Crude fiber.	N-free extract.	Total nitrogen.	Alb. nitrogen.
California	M. E. Jaffa, G. E. Colby.	11 09	5.42	2.90	9.18	24.34	58.17	1.47	1.18
Colorado	D. O'Brine	7.39	*4.16	4.06	7.40	*16,35	*68.03	.....	.....
Connecticut	Connecticut Agricultural Experiment Station.	7.88	5.82	2.47	8.47	22.61	60.63	1.36	1.23
	Storrs Agricultural School, C. D. Woods, H. B. Gibson.	8.55	5.76	2.38	9.13	22.89	59.84	1.46	1.10
Illinois	E. H. Farrington	10.00	5.78	2.07	8.46	22.02	61.67	1.35	1.18
Indiana	H. A. Huston	9.23	5.97	2.43	8.31	24.83	58.46	1.33	1.10
Kansas	G. H. Failyer, J. T. Willard.	9.47	5.47	2.28	8.80	23.67	59.78	1.41	1.14
Kentucky	A. M. Peters	9.33	5.85	2.06	8.63	24.18	59.28	1.38	1.17
Maryland	H. J. Patterson	10.60	5.07	3.47	.....	23.75	.....	.....	.....
Missouri	P. Schweitzer	9.67	6.36	1.88	8.85	23.22	†56.67	1.42	.....
	B. v. Herff								
New Jersey	L. A. Voorhees	8.50	5.79	2.52	8.88	22.33	60.48	1.42	1.30

* Not included in the above averages, and comparisons of results.

† We are informed by the author that a recalculation shows these figures to be in error; that the true number is 59.67.

HAY—Continued.

State.	Analyst.	Moisture.	In the dry substance.						
			Pure ash.	Ether extract.	Crude protein.	Crude fiber.	N-free extract.	Total nitrogen.	Alb. nitrogen.
New York	Cornell University, W. P. Cutter.	8.53	5.48	2.26	8.68	24.56	59.22	1.39	.....
	Cornell University, H. Snyder.	8.33	5.45	2.82	8.56	23.89	59.28	1.37	.....
North Carolina	B. W. Kilgore	8.91	6.29	3.21	7.81	26.90	55.79	1.25	1.16
Pennsylvania	W. Frear, A. Fries, H. B. McDonnell.	9.12	5.83	*5.60	8.94	24.89	55.54	1.43	1.09
	H. P. McDonnell	8.39	5.67	4.08	8.81	23.63	57.81	1.41	1.18
Texas	D. Adriance	*15.26	6.82	4.26	*12.18	*29.33	*47.41	*1.95	.....
U. S. Department Agriculture.	Aug. E. Knorr, T. C. Trescot.	8.57	6.09	2.15	8.94	†18.76	†67.16	1.43	.....
Virginia	W. Bowman	8.77	5.50	3.00	8.66	23.42	59.41	1.38	1.24
West Virginia	H. R. Baldwin	7.11	6.25	2.49	8.30	20.49	62.47	.....	1.14
Averages		9.40	5.94	2.73	8.58	23.61	58.60	1.38	1.17
Difference between highest and lowest per cent		.....	1.75	2.20	1.78	6.41	6.93	.....	.....
This difference expressed in per cent of average		.....	29.5	80.6	20.7	27.2	11.8	.....	.....
Widest difference from average		.....	.88	1.35	1.18	3.29	3.87	.....	.....
This difference expressed in per cent of average		.....	14.8	49.5	13.8	13.9	6.6	.....	.....

WHEAT MIDDLINGS.

California	M. E. Jaffa, G. E. Colby.	13.60	1.02	1.99	13.59	0.86	82.54	2.18	1.84
Colorado	D. O'Brine	9.91	1.22	2.55	*9.62	*2.90	83.71	.....	.....
Connecticut	Connecticut Agricultural Experiment Station.	11.06	0.96	1.91	13.00	1.36	82 77	2.07	2.03
	Storrs Agricultural School, C. D. Woods, H. B. Gibson.	11.65	0.94	1.73	13.13	0.62	83.58	2.10	1.96
Illinois	E. H. Farrington	12.40	0.80	1.55	13.13	0.96	83 98	2.10	1.70
Indiana	H. A. Huston	9.63	1.18	2.67	12.16	0.70	83.56	1.95	1.94
Kansas	G. H. Failyer, J. T. Willard.	11.75	0.84	1.78	12.61	0.79	83.29	2.02	1.62
Kentucky	A. M. Peters	12.25	0.92	1.82	12.81	0.62	83.83	2.05	1.81
Maryland	H. J. Patterson	11.95	0.91	1.93	.....	0.98	.....	.....	.....
Missouri	P. Schweitzer	13.27	1.14	1.73	13.25	0.64	83.24	2.12	.....
	B. v. Herff								
New Jersey	L. A. Voorhees	10.70	0.96	1.87	12.98	0.69	83.50	2.08	2.05
New York	Cornell University, W. P. Cutter.	9.77	*2.55	1.74	12.96	*2.51	*80.24	2.07	.....
	Cornell University, H. Snyder.	9.84	0.84	1.76	12.70	0.86	84.04	2.03	.....
North Carolina	B. W. Kilgore	11.51	1.18	1.97	11.68	1.17	84.00	1.87	1.74
Pennsylvania	W. Frear, A. Fries, H. B. McDonnell.	.....	1.14	2.01	13.37	0.73	82.75	2.14	1.95
	H. B. McDonnell	10.77	1.01	2.11	12.06	0.69	84.13	1.93	1.89
Texas	D. Adriance	14.57	1.01	2.10	12.12	0.89	83.89	1.94	.....
U. S. Department of Agriculture.	Aug. E. Knorr, T. C. Trescot.	11.70	0.95	2.15	13.09	0.63	85.12	2.10	.....
Virginia	W. Bowman	11.52	1.03	2.25	12.33	0.67	83.72	1.99	1.99
W. Virginia	H. R. Baldwin	8.09	0.90	2.74	.....	0.75	.....	.....	1.77
Averages		11.32	0.99	2.02	12.79	0.71	83.63	2.04	1.92
Difference between highest and lowest		.....	0.42	1.19	1.91	0.74	2.58	.....	.....
This difference expressed in per cent of average		.....	42.4	58.9	14.9	104.2	3.08	.....	.....
Widest difference from average		.....	0.23	0.72	1.11	0.65	1.49	.....	.....
This difference expressed in per cent of average		.....	23.2	35.6	8.7	91.6	1.8	.....	.....

*Not included in the above averages and comparisons of results.
†Not included in the above averages and comparisons of results, 5 per cent acid and alkali having been used in the treatment for the fiber.

LINSEED MEAL.

State.	Analyst.	Moisture.	In the dry substance.						
			Pure ash.	Ether extract.	Crude protein.	Crude fiber.	N-free extract.	Total nitrogen.	Alb. nitrogen.
California	M. E. Jaffa, G. E. Colby.	10.99	5.66	9.91	42.62	8.40	33.42	6.82	6.45
Colorado	D. O'Brine	8.04	5.40	*11.15	*28.66	8.82	*46.03	.....	.....
Connecticut	Connecticut Agricultural Experiment Station.	9.02	6.10	9.71	41.08	8.08	35.03	6.57	6.20
	Storrs Agricultural School, C. D. Woods, H. B. Gibson.	9.23	5.87	9.48	41.63	7.49	35.53	6.66	6.37
Illinois	E. H. Farrington	9.88	6.30	9.33	41.40	7.67	35.30	6.62	5.70
Indiana	H. A. Huston	7.81	6.11	9.90	39.45	7.64	36.90	6.35	6.30
Kansas	G. H. Failyer, J. T. Willard.	9.03	5.74	9.62	40.50	7.52	36.62	6.48	6.01
Kentucky	A. M. Peters	9.57	6.00	8.86	40.06	7.59	34.49	6.41	5.93
Maryland	H. J. Patterson	10.00	5.57	9.99	.....	7.57	.....	.....	.....
Missouri	P. Schweitzer	10.25	6.43	9.24	41.06	7.43	35.84	6.57	.....
	B. v. Herff								
New Jersey	L. A. Voorhees	8.49	6.01	9.59	40.64	7.21	36.55	6.50	6.32
New York	Cornell University, W. P. Cutter.	6.85	5.17	9.46	38.66	9.01	38.70	6.18	.....
	Cornell University, H. Snyder.	8.15	5.43	9.90	41.18	7.20	36.29	6.55	.....
North Carolina	B. W. Kilgore	9.65	6.18	9.98	37.12	7.98	38.74	5.94	5.51
Pennsylvania	W. Frear, A. Fries, H. B. McDonnell.	.....	6.02	9.58	39.06	7.81	37.53	6.25	6.26
	H. B. McDonnell	8.70	5.61	9.63	40.69	7.80	36.27	6.51	5.02
Texas	D. Adriance	12.79	6.36	9.86	41.18	9.61	32.99	6.59	.....
U. S. Department of Agriculture.	Aug. E. Knorr, T. C. Trescot.	8.91	5.92	9.29	41.25	7.37	41.91	6.60	.....
Virginia	W. Bowman	8.95	6.06	9.45	40.34	7.65	36.50	6.45	6.28
West Virginia	H. R. Baldwin	.....	.....	9.02	*55.97	*5.82	43.54	.....	5.11
Averages		9.25	5.89	9.57	40.77	7.41	36.82	6.48	5.95
Difference between highest and lowest		.....	1.26	1.12	5.50	2.41	8.92	.....	.....
This difference expressed in per cent of average		.....	21.4	11.7	13.5	32.5	24.2	.....	.....
Widest difference from average		.....	0.72	0.71	3.65	2.20	5.09	.....	.....
This difference expressed in per cent of average		.....	12.1	7.4	9.0	29.7	13.8	.....	.....

* Not included in the above averages and comparisons of results.

COMMENTS AND SUPPLEMENTARY INVESTIGATIONS BY THE SEVERAL ANALYSTS.

THE HYGROSCOPIC WATER.

Colorado.—A longer time was required to get a constant weight drying in hydrogen than in the usual way, from twenty to thirty minutes. On heating longer than three hours and twenty minutes, the sample increased in weight in every experiment.

Connecticut (Storrs School).—"The loss in weight at the end of five hours was considered to represent the moisture content of the samples. In the case of the middlings and linseed meal there was practically no loss in weight after five hours, but the hay continued to lose, and it was not dried to constant weight. Have always noticed this peculiarity in the drying of coarse fodders."

Missouri.—From the results of over sixty determinations of moisture the following averages are taken and conclusions drawn. The hydrogen and illuminating gas were passed through potassium permanganate and then dried before coming in contact with the substance.

Sample.	In hydrogen.			In illuminating gas.		
	1 hour.	2 to 3 hours.	Over 3 hours.	1 hour.	2 to 3 hours.	Over 3 hours.
Hay	9.50	9.67	9.79	9.77	9.63	9.73
Middlings	13.34	13.27	13.30	13.16	13.21	13.21
Linseed meal	10.27	10.25	10.26	9.94	9.97	10.02

"With air-dry fodder, drying for one to two hours is quite sufficient when dry hydrogen gas is used; a longer heating is disadvantageous to subsequent fat extraction. Where the drying is done in air, partial oxidation with consequent apparent decrease of water occurs, as seen in the following figures, obtained by drying the substance in air for four hours; the greatest apparent diminution being in middlings and linseed meal, probably because the fat is more readily oxidized than other constituents are."

	Per cent.
Hay	9.08
Middlings	12.17
Linseed meal	9.23

Some desiccator tests were made with one series of samples, giving a slight but continuous loss of moisture with increasing length of exposure in the desiccator, as shown by the following figures. The substance was first dried for two hours at the temperature of boiling water; the per cent of moisture thus found is given in the first column.

Sample.	Drying 2 hours.	Then in desiccator—			
		10 minutes.	20 minutes.	30 minutes.	2 hours.
In hydrogen:					
Hay	9.61	9.56	9.54	9.51	9.38
Middlings	13.14	13.10	13.07	13.05	12.90
Linseed meal	10.00	9.98	9.96	9.93	9.92
In illuminating gas:					
Hay	9.42	.....	9.41	.....	9.35
Middlings	13.10	.....	.....	13.05	.....
Linseed meal	9.86	9.85	.....	9.79	.....

Texas.—The hay was stated to be sour like ensilage when received. The very large per cent of moisture reported indicates that all the samples had been unusually exposed.

U. S. Department of Agriculture.—The results reported are the highest figures obtained by drying to constant weight, requiring twelve to sixteen hours. For practical purposes the analyst of the samples, Mr. Knorr, recommends seven hours as sufficient, the moisture being driven off to within 0.04 to 0.06 per cent and duplicates agreeing very closely.

THE ASH.

Kentucky.—The ash of the middlings and the linseed meal contained only traces of CO_2. In the ash of the hay the CO_2 was estimated by loss of weight of the apparatus.

Missouri.—The ash of the middlings and of the linseed meal contained no CO_2; that of the hay 0.38 per cent.

U. S. Department of Agriculture.—The determinations were made according to the old method, incinerating to whiteness at the lowest possible temperature.

THE ETHER EXTRACT.

Kansas.—An all-glass syphoning extractor was used.

Kentucky.—Besides using the official method, trials were made on the substance dried in a watch glass in the air, and in every case the results were lower, being 8.46 per cent for the hay, 10.47 for the middlings, and 8.26 for the linseed meal. With one sample of linseed meal 8.86 per cent of extract was obtained; it was suspected that the supply of hydrogen gave out during the desiccation, and that the result would prove to be too low. On bringing all the results together, obtained by the different analysts, this proved to be the case, and it was therefore left out by the reporter.

The determination of the ether extract by loss of weight of the extraction tube (Caldwell's) gave in all cases a lower result—1.98 for the hay, 1.13 for the middlings, and 8.32 for the linseed meal.

Maryland.—The results on ether extract purified by animal charcoal were, on hay 3.07, middlings 1.71, and linseed meal 8.91 per cent.

Illinois.—The ether extract was not dried in hydrogen.

Missouri.—From the results of over one hundred experiments the following averages are given and conclusions drawn. The anhydrous ether used was "made in the laboratory from stronger ether freed from alcohol by washing; requires much precaution to keep it from absorbing moisture; a chloride of calcium tube was attached to the upper end of the condenser."

The extraction tubes with the extracted substance were dried in hydrogen and weighed, giving the ether extract by loss of weight as well as by direct weighing of the extract.

In the following table the effect of different times of extraction is shown, the time being given in hours:

Name of substance.	Anhydrous ether, substance dried in—				Stronger ether, substance dried in—				Petroleum ether, substance dried in—			
	Hydrogen.		Illuminating gas.		Hydrogen.		Illuminating gas.		Hydrogen.		Illuminating gas.	
	Time of extract.	Per cent of extract.	Time of extract.	Per cent of extract.	Time of extract.	Per cent of extract.	Time of extract.	Per cent of extract.	Time of extract.	Per cent of extract.	Time of extract.	Per cent of extract.
Hay	13	1.70	13	1.69	8	3.09	8	2.98	12	1.28	12	1.32
Do	60	1.89	60	1.88	63	5.84	54	5.42	60	1.31	60	1.35
Middlings	13	1.50	13	1.48	8	1.62	8	1.55	12	1.30	12	1.14
Do	60	1.55	60	1.53	63	2.10	63	2.05	60	1.31	60	1.32
Linseed meal	13	8.29	13	8.32	8	8.62	8	8.70	12	7.58	12	8.01
Do	60	8.38	60	8.41	54	9.45	63	9.60	60	8.00	60	8.03

The difference between the two series with anhydrous sulphuric ether and with petroleum ether ranges from 0.24 to 0.48 per cent, and is always in favor of the sulphuric ether.

It is plain that anhydrous ether is the best medium for extracting fat, and that the extraction is complete at the end of thirteen or, say, fifteen hours; a longer treatment removes only small portions of resinous or waxy matters, but no fat. Petroleum ether is not so effective, requiring in the first place a longer time for action, and leaving behind, in the second place, a portion of the fat, or of the resin and wax heretofore counted as fat. For that reason I consider the first set of figures to give the correct values for the two solvents, and reject the figures obtained in the hydrogen and gas-dried material with stronger ether. Successive extractions made with the latter seem to increase the water in the substance and wash out sugar, as proven by test. Compensation of the errors might be effected by reducing the time for extraction from eight to six hours or drying the material as well as the extracted matter in air instead of hydrogen or gas. A determination made in this way gave the following results:

Per cent.		Per cent.
1. 2.29	....duplicate....	2.26
2. 1.49	....duplicate....	1.49
3. 8.54	....duplicate....	8.75

When the tubes containing the extracted substance were dried, with their contents, in hydrogen, or in illuminating gas, according as they were dried in one or the other at first, this determination of the extract by loss of weight gave results higher by

from 0.04 up to 0.34 per cent, this difference being less in the case of the extraction with petroleum ether than with either of the other extracting agents. A similar result was obtained in the laboratory at Cornell University. It is difficult to explain this divergence, and I do not know that we are in a position to decide which result is to be taken as the correct one, the direct or the indirect one.

In the above table the results are given only for the two extremes of time—the shortest time, and the sum of all the periods of extraction. With the anhydrous ether there were three successive extractions of the same portion of substance, the first for thirteen hours, the second for twenty-five hours, and the third for twenty hours, making the total about sixty hours, for which the second result was given. The quantities extracted in the second and third operations were very small for both anhydrous sulphuric ether and petroleum ether, usually less than 0.1 per cent, and in one case only, with linseed meal running up to 0.18 per cent; but the difference between this behavior and that with the Squibb's stronger ether was remarkable, as shown by the figures which are given below:

3.—*Squibb's stronger ether—first extraction for ten hours, and each subsequent extraction for seven hours.*

	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	3.09	0.52	0.19	0.48	1.02	0.54
2	1.62	0.05	0.10	0.06	0.14	0.13
3	8.62	0.19	0.10	0.19	0.05	0.30
4	2.98	0.53	0.24	0.47	0.34	0.86
5	1.55	0.00	0.15	0.05	0.12	0.08
6	8.70	0.23	0.17	0.05	0.23	0.22

U. S. Department of Agriculture.—Seven hours was found sufficient for the complete extraction, and "less would not probably be safe in all cases."

THE PETROLEUM ETHER EXTRACT.

California.—With these samples, as in many other cases in their experience, it has given poor results. The extract amounted to less than half of that resulting from the treatment with ordinary ether. "Somehow the petroleum product obstinately refuses to penetrate a number of materials as thoroughly as a solvent does that is more or less soluble in water."

Connecticut (New Haven).—"Have made previous comparisons of the solvent effect of various petroleum benzine fractions with ether and chloroform, and have found that the benzine in all cases extracts less than ether, but most certainly extracts chlorophyll as completely as ether. We considered therefore that it has no advantages, and some disadvantages."

Kentucky.—"The manipulation was not as satisfactory as with ordinary ether on account of the petroleum ether containing products varying several degrees in boiling point, although it had been refractionated between 40° and 45°."

Reports on petroleum ether extract.

	Hay.	Middlings.	Linseed meal.
Indiana	2.19	2.42	9.68
Kentucky	2.05	1.86	9.18
New York	1.63	1.66	9.05
Pennsylvania (McDonnell)	1.82 1.87	1.55 1.89	9.21 9.55
Virginia	2.30	2.06	9.84

Connecticut (*New Haven*).—Did not use blast, but were not troubled with foaming of the liquid. Were more troubled with bumping in the treatment with alkali on account of the presence of the asbestos and glass wool of the filter.

Connecticut (*Storr's School*)—Were quite unsuccessful in the use of the asbestos and glass-wool filter; used linen with more concordant results, and much more uniformly rapid filtration, in no case requiring more than four minutes, while the time required for the filtration with the asbestos and glass-wool filter ranged from four minutes to six hours for the acid extract, and three to thirty minutes for the alkaline extract. With the linen filter ten minutes is sufficient time in which to make the filtration from the acid solution, wash the residue, transfer to the flask, and bring the alkali to boiling. The filtration from the alkaline extract is made on linen, and then a transfer is made to a Gooch crucible, so as to insure perfect washing. On two hundred determinations of fiber in that laboratory the time necessary for completing duplicate analyses, from boiling of acid to putting washed crude fiber in the drying oven, varied from one and one-half to one and three-fourths hours.

One trial was made with linseed meal, using alkali first and the asbestos filter, but the filter became completely choked.

Indiana.—Used linen filters for both acid and alkali filtrations.

Kentucky.—The soda solution used contained a small quantity of carbonate.

Illinois.—The attempt to use the alkali first was a failure, on account of slow filtration.

Missiouri.—Some small variations were made in the treatment of the substance in the twenty-four determinations of fiber. In one series the residue from the extraction of the substance dried in hydrogen or in illuminating gas with anhydrous ether was treated with a sodium hydrate free from carbonate; in another series it was the residues from the treatment with Squibb's stronger ether, using a sodium hydrate not free from carbonate; and in a third series the substance was originally dried in air, otherwise treated as was the second.

The results with the second series were slightly higher and those with the third and slightly lower than with the first, but the difference was in no case greater than 0.78 per cent on the hay, was not over 0.2 per cent with the middlings, and but a trifle over 0.3 per cent on the linseed meal, insignificant compared with the variations on the same sample by different analysts.

North Carolina.—The trial of the plan of treating first with alkali and then with acid gave no advantage, except with the middlings, when it was more satisfactory.

Pennsylvania.—The results on fiber were obtained by two analysts, each getting a number of closely agreeing duplicates, with manipulation essentially the same, but differing on the hay by 0.8 per cent; this is quoted by Mr. Frear as illustrating the difficulty of the determination.

Mr. McDonnell used for his filter a perforated platinum cone in an ordinary funnel covered with an asbestos welt.

Texas.—The boiling was done in an open Erlenmeyer flask.

United States Department of Agriculture.—It was found next to impossible to filter the solutions with the acid and alkali of official strength. The opinion is given that "so weak an acid will not saccharify all the starch of so farinaceous a substance as the middling in half an hour. Therefore 5 per cent solutions were used, as formerly in the laboratory of the Department, and no further trouble was encountered."

A comparison of the percentage statements of the divergence of results at the close of each table with the corresponding statements of last year does not give evidence of any satisfactory progress toward closer agreement between the results obtained by different analysts. Last year I expressed the opinion that the difference between the lowest and highest result on any one constituent should not exceed 15 per cent of the average, and that 10 per cent should be the limit for the widest variation above or below the average.

In making these calculations last year no results were rejected; this year I did not include those very small in number, which differed so widely from all the others of the same series that they could reasonably be regarded as incorrect; but notwithstanding this advantage given to the results of this year, the showing for them is better only in a few instances, and is worse in the majority of them, only those series being compared for which the calculations have been made in both years.

Last year some deviations from the official method were considered as possibly of sufficient importance to account for such serious discrepancies in the results; therefore strict adherence to the official method was specially requested by the reporter in the work of this year. Nevertheless the extreme variations are still just as wide or wider.

PART III.

This serious and persistent want of agreement between results may be due to three causes: First, incomplete mixing of the mass of ground material before taking out the several samples; second, imperfections of the methods of analysis; third, inexperience or carelessness in the execution of the work.

As to the first cause suggested, incomplete mixing, if it be this, then we may well doubt the sufficiency of any sampling of a large mass of fodder, if no dependence can be placed on uniformity of composition of a mass of fine powder treated as these samples were prepared. Further, it is easy to select several series of results on one constituent that agree fairly well while there are wide discrepancies in the results obtained by the same analysts on some other constituent; it would be reasonable to suppose that any want of uniformity in the samples would affect all the constituents.

In order to test this important matter your reporter would recommend that a portion of the ground substance, prepared for the analysis in the same manner as this year, be subjected to further mixing in a slowly revolving rectangular box not more than one-third or one-half filled with the powder, the revolution being continued for several hours, and that samples of this portion be sent out as well as of the other.

As regards the second possible cause, imperfections in the methods of analysis, it is reasonable to suppose that every sample would be affected alike when the same methods manipulated in the same way are strictly followed by all analysts. Little satisfaction appears to be gained in attributing the discrepancies to this cause.

As regards the third reason suggested, some of the widest variations from the average are reported by those whose experience and carefulness can not be reasonably questioned; and it is altogether too much to ask of the "personal equation" that it shall bear the blame for such wide discrepancies as may be found scattered through these tables. To your reporter it appears that there is nothing else to do than to await further developments from continued work along these lines.

The late date at which many of the reports were sent in, accompanied by regrets that the work could not have been completed sooner, indicates that there was difficulty in finding adequate time for it.

Your reporter therefore suggests that for the coming year some two or three constituents only be determined, as the ether extract, with which the determination of the moisture is easily combined, and possibly the fiber also, and that at the most two substances be sent out, or perhaps even only one, as some coarse fodder, that being the kind of material upon which there is the most serious disagreement.

Two distinct purposes may be accomplished by this analytical work that the association is doing; one to learn what methods will give concordant results when manipulated by experienced and careful analysts; the other to afford opportunity to the Experiment Stations to test the reliability of their less experienced assistants in the laboratory. If the accomplishment of the first purpose is the only one sought for, and the work is therefore done only by experienced analysts, we may hope to make some decided progress from year to year, and eventually attain the desired goal. Methods of analysis may then be laid down which we can be assured will give concordant results if properly carried out, or else we shall have learned that such methods are unattainable. In either case we shall have completed our work.

If the second purpose is the one to be accomplished, your reporter does not see what is to save us from going on from year to year as we have been going in the years past, making very slow progress towards definite results, because at least some of the work, while perhaps as good as could be expected for its kind, is not of the kind that helps us to decide whether a method is to be accepted or rejected, because it is not experienced work, and therefore is not reliable work for the purpose in view.

Your reporter therefore recommends that, at least so far as concerns this branch of our work, the coöperation be sought of only a small number of analysts, say ten or twelve, experienced in the analysis of fodder, or of unquestionable reliability in any kind of agricultural chemical analysis, rather than to extend the invitation to all experiment stations. All the results sent in would then be useful, and in equal degree.

Your reporter also recommends that comparative tests be made of Patterson's purification of the ether extract by animal charcoal.

Your reporter further gladly accepts the recommendation made by a member of the association that besides making the ether extraction of the substance dried in hydrogen, it be made also on the substance as received.

It was directed by the association that all samples be sent out in sealed glass bottles, and that reports be sent in on the analysis of the substance as received, thus controlling the determination of the moisture as well as the other constituents determined.

Mr. Huston presented the following paper:

NOTES ON THE ANALYSIS OF CATTLE FOODS.

By H. A. Huston.

The following investigations were undertaken as preliminary to a more extended study of the present methods of cattle food analysis. The object in view was to determine—

(1) The influence of complete or nearly complete drying on the amount of crude fat extracted by absolute ether and petroleum spirit.

(2) A comparison of petroleum spirit and absolute ether as solvents of crude fat.

(3) The influence of water on the amount of the ether extract.

(4) The influence of small amounts of alcohol on the amount of ether extract.

(5) The effect of reversing the order of application of the solvents used to determine crude fiber.

(6) Study of the temperature to be used in the final drying in the determination of ash.

The material used was the set of samples sent out by the cattle food reporter of the Association of Official Agricultural Chemists, 1889–'90, viz: Hay, wheat, middlings, linseed meal. The sample of clover is one raised on the farm of the Indiana Agricultural Experiment Station.

The hay contained 9.23 per cent water, the middlings 9.63 per cent, the linseed meal 7.81 per cent, and the clover 11.25 per cent. The results are for these air dried substances. The solvents used, the time and temperature of drying are stated in the table. The dryings in the desiccators were at the room temperature during the winter, with thermometer ranging from 55° to 75° F. Each sample was in a separate desiccator over C.P. sulphuric acid. The material was on watch glasses, and was weighed from time to time, and was protected from the air during the weighing. The first weighing was made after twenty days, and over 90 per cent of the water was removed in this time. The duplicates, however, varied too widely to make this a desirable method for determining water. Experiments on mixed hay and clover showed that the drying is nearly complete in seven days over sulphuric acid, and

that calcium chloride is not suitable for such work. The drying in hydrogen was conducted in a bath of hot water boiling at 100° C. The material was contained in glass tubes 19 centimeters long and 1.5 internal diameter, with a small tube 1 centimeter long sealed to the bottom. This small tube was used to make the connection with the hydrogen-distributing apparatus which had an independent stopcock for each of the eight tubes which it supported.

The time of extracting was forty-eight hours in all cases excepting the clover. The clover was extracted twenty-four hours. In the other cases the material was extracted for twenty-four hours, and the amount of extract determined. It was then extracted for another period of twenty-four hours, and the sum taken as the extract. Soxhlet's apparatus was used throughout. Part of the extractors were of the ordinary type, with cork joints, and part were of my own design, with glass joints throughout. Repeated blank experiments failed to give any residues where cork joints were used. The condensers were about 1 meter long, and the tops were closed with closely fitting inverted test tubes. The tubes in which the material was dried were placed in the extractors, plugs of thoroughly extracted absorbent cotton being used above and below the material. In petroleum spirit extractions the substances were held down by pieces of heavy glass tubing placed over the material in the containing tube. The additional space in the extractors was filled with glass rods. When the extractions were finished the tube and rods were removed and the extractor used as a recovery apparatus for the ether. In case of petroleum a special recovery apparatus was found necessary.

The ether used had been standing over metallic sodium for some months, and was distilled as needed. The petroleum spirit had been obtained by taking the fraction distilling between 40° and 50° C. on the second distillation. This is much to be preferred to that coming over between 40° and 50° on the first distillation, as the latter contains considerable material boiling between 32° and 40°, and this gives rise to considerable trouble in the extraction. The extracts were dried at 100° C. in a current of dry hydrogen.

The results appear in the following table:

Number.	Method of drying.	Solvent.	Hay.			Wheat middlings.		
			Loss on drying.	Extract.	Sum of loss on drying and extract.	Loss on drying.	Extract.	Sum of loss on drying and extract.
1	120 days in desiccator over sulphuric acid.	Petroleum spirit	7.225	1.425	8.650	10.665	1.752	12.417
2	....do	Absolute ether	7.055	1.665	8.720	10.760	1.740	12.500
3	4 hours in hydrogen at 100° C.	Petroleum spirit	7.810	1.993	9.803	8.650	2.190	10.840
4	....do	Absolute ether	7.658	2.210	9.868	9.570	2.422	11.992
5	48 hours in hydrogen at 100° C.	Petroleum spirit	8.710	1.593	10.303	9.633	0.780	10.413
6	.. do	Absolute ether	9.230	1.870	11.100	10.645	1.060	11.705
7	225 hours in hydrogen at 100° C.	....do	.....	.....	.....	.....	.....	.....
8	4 hours in hydrogen at 100° C.	Absolute ether + 3½ per cent absolute alcohol.	.....	2.395	.....	.....	1.690	.....
9	....do	Absolute ether + water equal to loss of water on drying the sample.	7.600	2.220	9.820	11.020	1.865	12.885
10	Not dried	Petroleum spirit	.....	1.865	.....	.....	2.100	.....
11	....do	Absolute ether	.....	2.410	.....	.....	2.195	.....
12	....do	Water-saturated ether, pure.	.....	3.625	.....	.....	1.925	.....
13	....do	Residue from No. 11 extracted with absolute ether + 3½ per cent absolute alcohol.	.....	3.210 (0.800)	.....	.....	2.510 (0.315)	.....
14	....do	Absolute ether + 3½ per cent absolute alcohol.	.....	3.590	.....	.....	2.155	.....

Number.	Method of drying.	Solvent.	Linseed meal.			Clover.		
			Loss on drying.	Extract.	Sum of loss on drying and extract.	Loss on drying.	Extract.	Sum of loss on drying and extract.
1	120 days in desiccator over sulphuric acid.	Petroleum spirit	7.880	6.615	14.495	.....	.....	.....
2	....do	Absolute ether	7.793	6.825	14.618	.....	.....	.....
3	4 hours in hydrogen at 100° C.	Petroleum spirit	8.023	8.932	16.955	9.050	1.580	10.630
4	....do	Absolute ether	7.513	9.122	16.635	9.168	2.222	11.390
5	48 hours in hydrogen at 100° C.	Petroleum spirit	7.813	2.767	10.580	.....	.....	.....
6	....do	Absolute ether	7.705	4.847	12.552	.....	.....	.....
7	225 hours in hydrogen at 100° C.	....do	.....	.....	.....	11.250	1.432	12.682
8	4 hours in hydrogen at 100° C.	Absolute ether + 3½ per cent absolute alcohol.	.....	9.050	.....	.....	2.080	.....
9	....do	Absolute ether + water equal to loss of water on drying the sample.	7.630	8.610	16.240	.....	.....	.....
10	Not dried	Petroleum spirit	.....	9.385	.....	.....	1.820	.....
11	...do	Absolute ether	.....	9.485	.....	.....	2.885	.....
12	....do	Water saturated ether, pure.	.....	9.659	.....	.....	4.460	.....
13	....do	Residue from No. 11 extracted with absolute ether + 3½ per cent absolute alcohol.	.....	9.975 (0.495)	.....	.....	3.995 (1.110)	.....
14	....do	Absolute ether + 3½ per cent absolute alcohol.	.....	9.590	.....	.....	4.390	.....

In this table only the means are given. The table shows that long drying of the samples, either in desiccators or in hydrogen, results in a very marked diminution of the amount of matter extracted either by petroleum spirit or by ether. Compare No. 1 with No. 3, No. 2 with No. 4, No. 3 with No. 5, No. 4 with No. 6.

On comparing No. 3 with No. 10 and No. 4 with No. 11 it is seen that there is relatively little difference between the extract from samples dried four hours at 100° in hydrogen and from the substances in the air-dried condition. No. 9, in which the substance was first dried four hours in hydrogen at 100°, and then water added equal to the loss on drying, shows the same thing.

No. 8 seems to indicate that if the substance be previously dried the addition of 3½ per cent of alcohol to the ether makes comparatively little difference, while Nos. 13 and 14 show that in case of substances containing considerable chlorophyll the addition of alcohol makes a marked increase in the amount of extractive matter. In the same way No. 12 shows that the presence of an excess of water in the ether makes a decided increase of extractive matter in case much chlorophyll is present, but comparatively little difference in the case of other substances. No. 13 was intended to show whether the same results would be obtained by extracting the substance with two solvents successively as would be obtained on direct extraction with the second solvent, as in No. 14. In No. 13 the upper row of figures is the sum of the absolute ether extract obtained in No. 11 and the amount obtained by subsequent extraction with alcoholic ether. The lower row of figures is the amount of extract by the alcoholic ether. The results of a number of comparisons between Squibb's stronger ether and absolute ether show that in every case Squibb's ether gives an amount of extractive matter far greater than would be accounted for by the amount of alcohol present in it. The Squibb's ether had been redistilled, and the distillate left no residue on evaporation.

The column headed "Sum of loss on drying and extract" is entered to show that the reduction of extractive matter is not wholly due to loss through volatilization of material on drying.

The chief cause of the smaller amount of extractive matter in the samples submit-

ted to long drying is probably, as suggested by Dr. Wiley, a change in the cell wall by which the inner layer of nitrogenous material becomes less pervious to the fluids used as solvents. This matter is now being investigated.

The fact that long drying has the same effect in the case of fungi containing no true cellulose seems to confirm this view.

It is noteworthy that if the comparisons of extractive matter in the samples that have been dried four hours and in the air-dried samples be made on the amount extracted in the first twenty-four hours instead of in forty-eight hours, the differences almost disappear; but the ratio between the amounts dissolved by petroleum spirit and absolute ether remains practically the same.

In all cases where any examination of the material extracted during the second period of twenty-four hours was made the extract did not appear to have the properties of fatty substances; but the amounts obtained were so small as to render any complete examination impossible.

CRUDE FIBER.

The results of applying the alkali first in the determination of crude fiber showed that in every case there was a loss of time; with wheat middlings this loss amounted to six hours, and with the linseed meal to four days. In all cases a higher per cent. of fiber was obtained than by the official method, and the duplicates varied more widely.

ASH.

In the determination of ash I have frequently noticed that the charred mass when treated with water gives a brownish colored solution. Moreover, the drying at 110° C. would not remove all the water of crystallization should any be present, nor would it remove the brown, caramel-like substance contained in the solution. The following results were obtained, using higher temperatures:

	Per cent of ash.		
	Hay.	Middlings.	Linseed meal.
Dried at 110° C	5.42	1.07	5.64
Dried at 230° C	5.27	0.96	5.53
Ignited one to two minutes at very low red heat*	5.05	0.86	5.34

* This is the method adopted for the coming year.

Mr. Anderson presented the following paper:

EXPERIMENTS IN DETERMINATION OF MOISTURE, AND ETHER EXTRACT.

By J. T. Anderson.

In December of last year Professor Caldwell issued his bulletin describing "A new apparatus for drying substances in hydrogen, and for the extraction of fat." This apparatus was procured for our laboratory at once, and with it a series of experiments was instituted, some of whose results the writer deems of sufficient interest to bring to the attention of this association. It was proposed to compare the old method of drying in air with the newer one of drying in hydrogen. That the temperature might be the same in all cases, the drying, whether in air or hydrogen, was conducted in a water bath of boiling water. Cotton-seed meal and German millet were the substances selected for the experiments. With the cotton-seed meal the mean of six determinations of moisture by drying in air gave 8.81 per cent. The mean of seven determinations in hydrogen was 9.73 per cent, making a difference of 0.92 per cent in

favor of drying in hydrogen. With German millet similar results were obtained. The mean of four determinations in air gave 10.53 per cent H_2O, in hydrogen 10.73 per cent H_2O, a difference of 0.20 per cent in favor of drying in hydrogen. These results were not unexpected, but are given as confirmatory of the opinion generally entertained, that we do not get the full amount of moisture in feed stuffs when we dry them in air, since the loss of weight after drying does not represent the weight of the moisture driven off.

Some interesting facts were elicited in the matter of determining the ether extract. As a matter of convenience it has been our custom in the Alabama laboratory to determine the ether extract by drying and weighing the residue of fiber, carbohydrates, etc., instead of the product extracted by the ether. This writer undertook some experiments recently to test the validity of this variation from the prescribed method. As in the moisture determinations, cotton-seed meal and German millet were the substances used. In all cases the extraction product and the residue left after the extraction were dried to a constant weight in the same water bath of boiling water. With cotton-seed meal the following are the means of seven determinations of ether extract. From weighing the fiber residue, 7.63 per cent; from weighing the extraction product, 7.45 per cent. Six samples of German millet, treated in the same way, gave: From weighing the fiber residue, 3.95 per cent; from weighing the extraction product, 3.57 per cent. In every case a larger per cent of ether extract was obtained by weighing the fiber residue. This is believed to be due to the volatilization of ethereal oils in the process of drying the product extracted by the ether. What will be the effect of drying both the residue and the extraction product in hydrogen instead of in air is a question of considerable interest.

Mr. Anderson exhibited and explained an extraction apparatus used by himself with good results.

Mr. Wiley presented the following paper, from the Chemical Division, Department of Agriculture.

ON THE METHODS OF ESTIMATION OF THE FATTY BODIES IN VEGETABLE ORGANISMS.

By Walter Maxwell.

These investigations have been conducted with the purpose of acquiring some further data showing the comparative proportions of matters which become separated from vegetable organisms by extracting with pure ether in variable durations of time. It has further been attempted to determine whether the whole of the substituted glycerides, or lecithines, do become separated by direct extraction with ether only.

The materials used in the work were pulverized to the greatest state of fineness, and the extractions were made with the Knorr extraction apparatus. The calculations are reduced to the standard of water-free material.

(*a*) The preliminary experiments which were made in order to establish the proportions of the vegetable matters separated by the action of pure ether in different durations of time are illustrated by the following results:

Cotton Seed.

Time.	Weight of material.	Weight of extract.	Per cent.
Hours.	*Grams.*	*Grams.*	
$8\frac{1}{2}$	4	1.472	37.39
10	4	1.491	37.87
15	4	1.511	38.38

These results give the average of a great number of analyses. Although an increased amount of substance becomes separated with an increased duration of the period of extraction, the proportion is small; and it is not apparent that the greater duration of time causes an increase in the fatty bodies only, as other matters can be affected by a very protracted boiling. For these reasons it has been resolved to estimate the amounts of the fatty bodies separated by extraction with pure ether in a duration of fifteen hours.

In considering the estimation of the proportions of glycerides and substituted glycerides which are contained in the ether extract, the presence of other bodies, which have been removed with the ether, make it impossible, in the absence of an absolute analysis of the extract, to determine accurately the comparative relations of those fatty bodies. The ether extractions of plant matters contain variable proportions of cholesterin and of, in some instances, solid hydrocarbons, which may constitute several per cent of the extract. However, although the percentage of glycerides can not be definitely estimated, the lecithines or substituted glycerides may be determined with absolute accuracy, as the estimation of these bodies rests upon the proportion of phosphorus present in the ether extract. The extract is combusted with mixed alkali salts by which the phosphorus present in the organic form as lecithine becomes fixed as an alkali phosphate, and is then determined as magnesium pyrophosphate, and the latter body being multiplied with the known Hoppe-Seyler factor, gives the exact amount of lecithine.

A further series of extractions was made of the pulverized cotton seed with pure ether for a period of fifteen hours and the total extract determined. The proportion of lecithine contained in the extract was estimated by the method already given, the residue of the extract being considered as glycerides and other bodies. The average of eight analyses gave the following results:

	Per cent.
Extract	38.46
Glycerides, etc	98.84
Lecithines	1.16

(*b*) It will be shown that the proportion of substituted glycerides stated, 1.16 per cent, does not represent the total lecithine present in the cotton seed.

The observation was made simultaneously by Prof. E. Shulze, Zurich, and W. Maxwell, Harvard College, that the substituted glycerides do not become wholly separated by extraction with ether, even in a great duration of time. It was found that if the material which had been already extracted with ether were further extracted with absolute alcohol another portion of substituted glycerides was obtained, which in most instances was greater than the amount separated by the ether. The process of the alcohol extraction consisted in merely extracting the material already treated with ether and evaporating off the alcohol and reëxtracting the alcohol extract residue with ether. The reason for taking up the lecithines out of the alcohol extract was that it has been observed that those lecithines which were originally insoluble in ether became soluble in that menstruum when previously acted upon by alcohol. The use of ether was further made in order to avoid any small portion of inorganic phosphates which might have been removed from the vegetable material by alcohol. It was found, however, that only a mere trace of mineral phosphates had been separated by the action of the alcohol.

The amount of the ether extraction of the alcohol extract in one hundred parts of the vegetable material with the proportion of lecithines was as follows:

	Per cent.
Extract	2.3
Lecithines in extract	16.6

A further comparison indicates the following:

	Extract.	Lecithines.	Glycerides, etc.
	Per cent.	*Per cent.*	*Per cent.*
Ether	38.46	1.16	98.84
Ether and alcohol	40.76	2.30	97.69

The proportion of lecithines to the total fatty bodies contained in the cotton seed is very small, yet it is seen that about 50 per cent of those substituted glycerides are left in the material after extraction with ether for a period of fifteen hours. If certain other varieties of seeds be considered, such as the legumes, pea, vetch, bean, Boston bean, etc., it is found that the total ether and alcohol extracts of those seeds are composed of lecithines varying from 25 to 45 per cent. It is thus apparent that, in the examples of seeds given, as far as 20 per cent to 25 per cent of the total fatty bodies can remain unseparated and undetermined when the material is extracted with ether only.

Mr. Wiley explained certain new forms of apparatus used in his laboratory as follows:

SOME NEW FORMS OF APPARATUS USED IN AGRICULTURAL CHEMICAL ANALYSIS.

A NEW FORM OF EXTRACTION APPARATUS.

In Fig. 6 is represented a new form of extractor, devised and made by Mr. A. E. Knorr, of my division, in which the use of corks or ground glass connections of any kind is entirely dispensed with. The operation of the apparatus will be understood by a brief description of its parts.

A is the flask containing the solvent, W a steam bath made by cutting off the top of a Winchester quart bottle and inverting it and conducting the steam into one of the tubes shown in the stopper while the condensed water runs out of the other. The top of the bath is covered with a number of concentric copper rings, so that the opening may be made of any desirable size. B represents the condenser, which is a long glass tube on which a number of bulbs have been blown, and which is attached to the hood for holding the material to be extracted, as represented at B′, making a solid glass union. Before joining the tube at B′ the rubber stopper which is to hold it into the outside condenser of B is slipped on, or the rubber stopper may be cut into its center and slipped over the tube after the union is made. In case alcohol is to be used for the solvent, requiring a higher temperature, the flask holding the solvent is placed entirely within the steam bath, as represented at A′.

A more detailed description of the different parts of the apparatus can be seen by consulting Figs. 7, 8, and 9. In A, Fig. 7, is represented a section of the flask which holds the solvent, showing how the sides of the hood containing the matters to be extracted pass over the neck of the flask, and showing at S a small siphon inserted in the space between the neck of the flask and the walls of the hood for the purpose of removing any solvent that may accumulate in this space. A view of the flask itself is shown at A′. This flask is made by taking an ordinary flask, softening it about the neck and pressing the neck in so as to form a cup, as indicated at A′, to hold the mercury which seals the union of the flask with the condenser. The flask is held in position by passing a rubber band below it, which is attached to two glass nipples blown onto the containing vessel, as shown in Fig. 6*b*. The material to be extracted may be contained in an ordinary tube, as shown in Fig. 8, which may be made from a test tube drawn out, as indicated in the figure, and having a perforated platinum disk sealed in it at D. The containing tube rests upon the edges of the

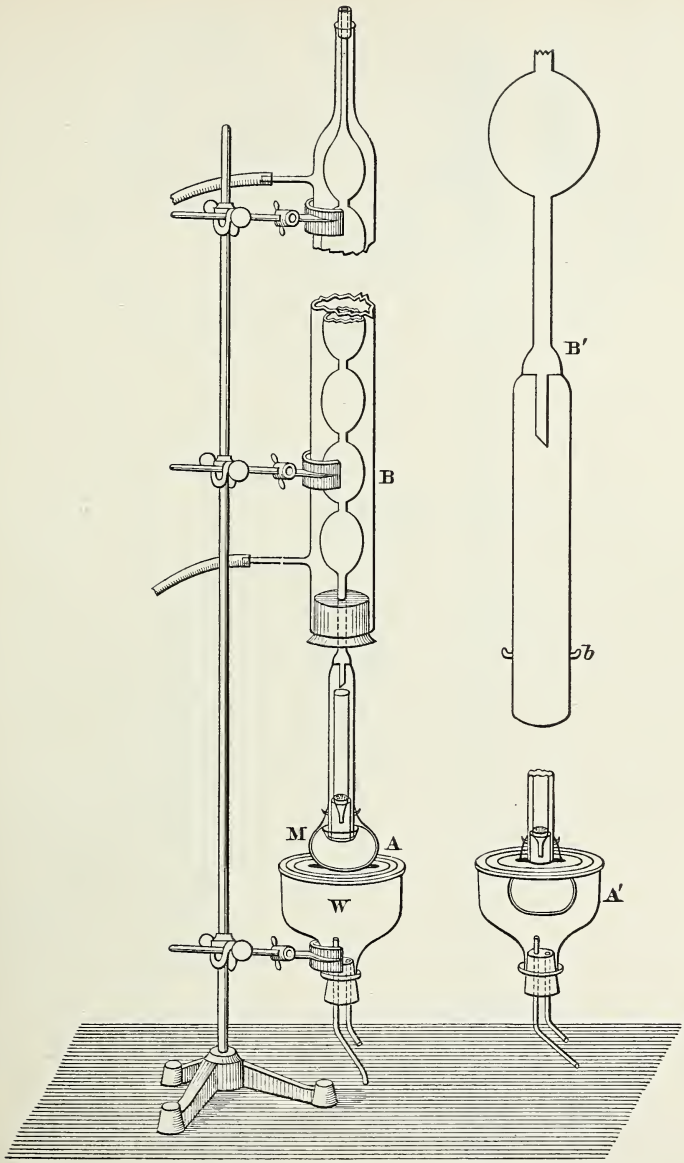


FIG. 6.

flask containing the solvent by means of the nipples shown at *t*. If a siphon tube is to be used, one of the most convenient forms, and one which is used exclusively in my laboratory, is shown in Fig. 9, in which the siphon lies entirely within the extracting tube, thus being protected from breakage. By means of this apparatus the extractions can be carried on with a very small quantity of solvent, there being scarcely any leakage, even with the most volatile solvents, such as ether and petroleum. The apparatus is always ready for use, no corks are to be extracted, and no ground-glass joints to be fitted. The apparatus has been in use for about a year, and has given most perfect satisfaction.

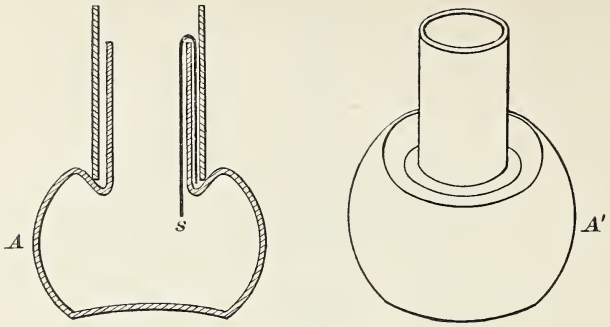


Fig. 7.

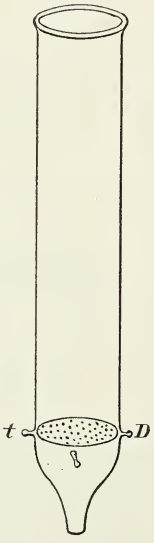


Fig. 8.

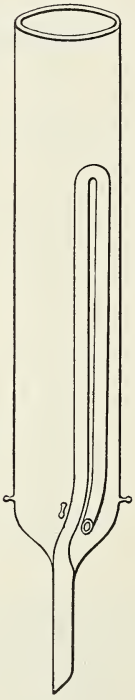


Fig. 9.

For the purpose of recovering the solvent the apparatus shown in Fig. 10 is used. W represents the steam bath, A the flask containing the solvent to be recovered, which is held in the usual way, connected with the condenser B by the bent tube, as shown, the condenser being connected with the flask R at G, and sealed into a cup similar to that used in the extractions at M by mercury.

In all cases after the apparatus is adjusted mercury is poured into the cup formed by the depression in the flask, thus sealing it completely and permitting the extraction to go on in an apparatus without a joint of any kind except that formed by the mercury in the cups.

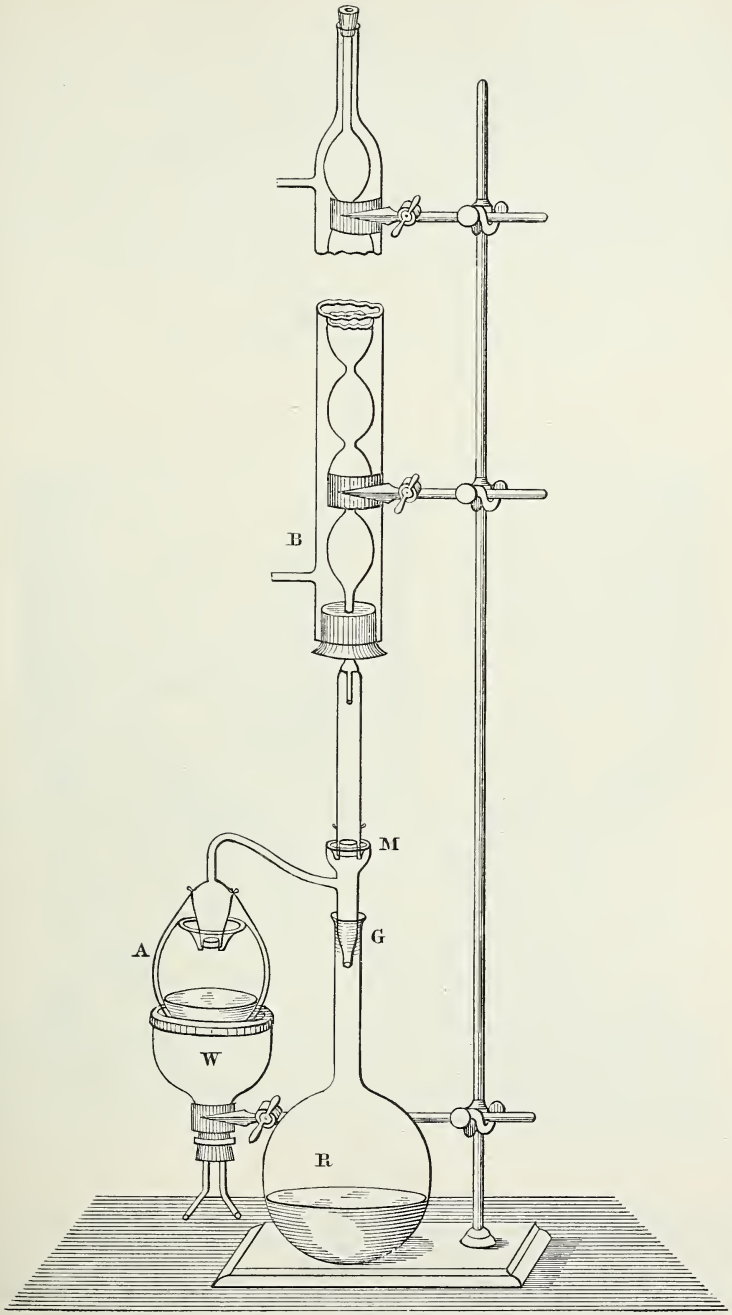


Fig. 10.

APPARATUS FOR DRYING IN HYDROGEN.

For the purpose of drying materials contained in flasks and tubes in a current of hydrogen the apparatus shown in Fig. 11 is used. This apparatus consists of a circular box, B, conveniently made of galvanized iron, having a movable cover, S, fitted for the introduction of steam into the interior of the apparatus. Condensed steam escapes as water at W. A stream of perfectly pure and dry hydrogen enters at H, passes up through the material to be dried, down through the bulb V, containing sulphuric acid, and following the direction of the arrows through the rest of the apparatus. The stream of hydrogen is thus completely dried by passing through bulbs containing sulphuric acid, and passing from one piece of the apparatus to the other.

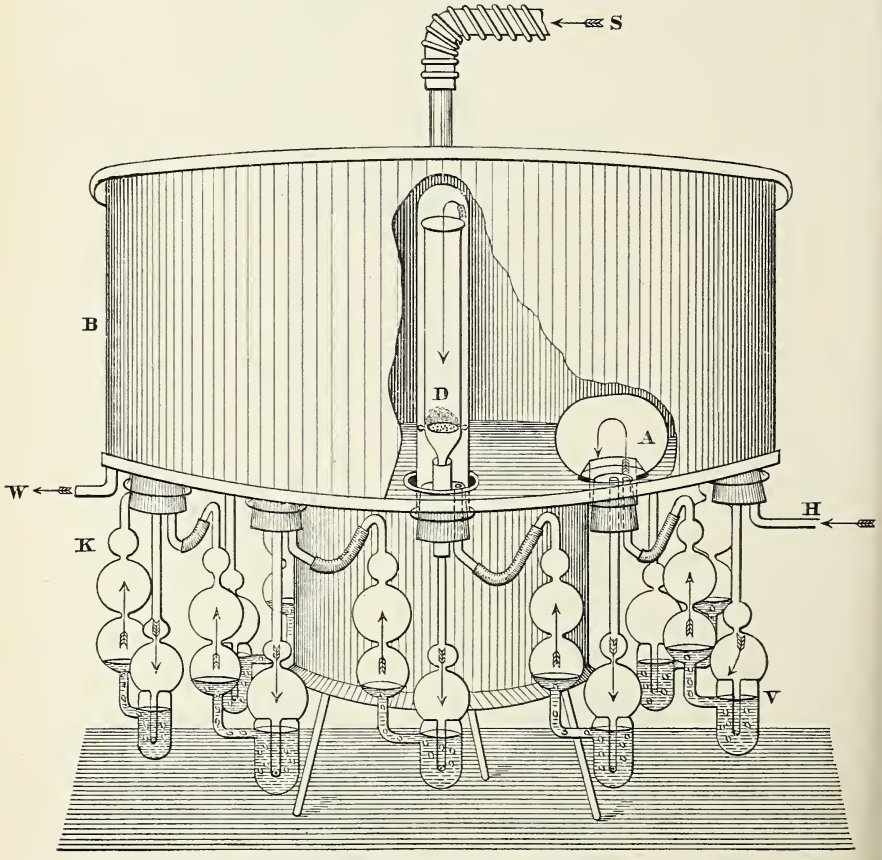


FIG. 11.

A, represents a flask such as is used, with the extraction apparatus described. The apparatus which we have used will hold eight tubes or flasks at a time, and thus a single stream of hydrogen is made to do duty eight times in drying eight separate samples. The great advantage of the apparatus is in the fact that we are absolutely sure of the stream of hydrogen passing over and through the substance to be dried. In order to prevent any sulphuric acid from being carried forward into the next tube we have decided to place an additional bulb at a point, K, above the sulphuric acid, and in this bulb solid pieces of soda or potash will be placed.

We have used this apparatus for nearly a year, and have not had any accidents from sulphuric acid being carried forward, and there is no danger, provided the stream of hydrogen is kept running at a slow rate. If, however, by any accident the stream of hydrogen should be admitted with great rapidity, particles of the sulphuric acid might be carried forward and spoil the next sample. To avoid any such accident as this the proposal to introduce the potash bulb has been made. The apparatus works with perfect satisfaction, and it is believed that when properly adjusted check weighings can be made by weighing the bulbs, showing their increase in weight, which will give the volatile matter, and weighing the flasks or tubes, which will show the loss of weight. The only chance for error in weighing the bulbs is that some of the volatile matter may be material which is not dissolved in sulphuric acid, and is thus carried on and out of the apparatus. The blackening of the sulphuric acid in the bulbs in the drying of all forms of organic matter shows that the loss in weight of such bodies is not due to water alone, but to organic volatile substances, which are capable of being decomposed by the sulphuric acid, thus blackening it.

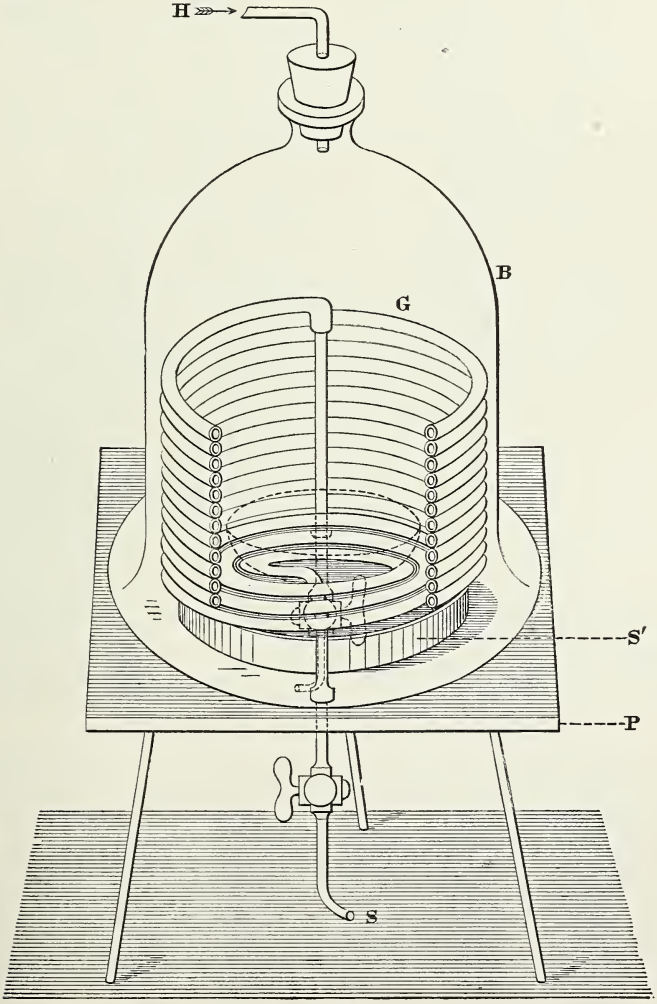


FIG. 12.

Fig. 12 shows another form of apparatus for drying in hydrogen, which is used for the purpose of drying substances in flasks, dishes, etc., in considerable numbers. It consists of an iron plate, P, smooth on upper surface, supported on three legs. This plate carries two perforations in the center, one for admitting the steam S, and the other for carrying off the products of condensation. Over the iron plate is placed a large bell-jar B, into which a stream of perfectly dry and pure hydrogen is admitted at H. The bell-jar fits snugly on the iron plate, and the stream of hydrogen is first admitted rapidly until all the air within the bell-jar is expelled. After this the stream of hydrogen is admitted slowly, so as to simply supply the place of hydrogen which may be lost by diffusion or leakage between the edges of the bell-jar and the iron plate. Within the bell-jar the copper or brass coil C is found, consisting of small brass or copper tubing coiled over the bottom at a distance of about 4 or 5 centimeters from the iron plate and then continued in a coil up the sides, as shown in the figure. Beneath this coil is a vessel, S′, containing strong sulphuric acid. The vessel to be dried, as shown in the figure, is placed within the coil, and is thus kept at a temperature of steam at whatever pressure it may be, while at the same time a slow current of dry hydrogen is passing over it. The space within the coil may be entirely filled with samples to be dried. The vapor of water, being heavier, rapidly falls through the hydrogen and is absorbed by the sulphuric acid in S. By varying the pressure of the steam admitted the temperature of air within the coil may be kept at various points from 98° up to even 103°. It is not difficult to secure within this coil the temperature of boiling water, and thus have the dishes containing organic matter dried in a perfectly dry atmosphere of hydrogen.

DEVICE FOR RECOVERING SOLVENTS FROM OPEN DISHES.

It often happens that materials which are dissolved by the ordinary solvents in use are to be collected in open dishes in order that their properties may be studied. At the same time large quantities of solvent must be used, and it is desirable to have some method of recovering such solvents. The device shown in Fig. 13 has been found to work excellently well for this purpose. It consists of a steam bath, W, and a bottle, B, with the bottom cut off, resting on an iron dish P, containing a small quantity of mercury, enough to seal the bottom of the bottle. The dish containing the solvent is placed on the mercury, and the bottle placed down over it, forming a tight joint. On the application of steam the solvent escapes into the condenser C, and is collected as a liquid in the flask A. In very volatile solvents the flask A may be surrounded with ice, or ice-cold water passed through the condenser. When an additional quantity of the solvent is to be added to the dish for the purpose of being evaporated it is poured in the funnel F, and the stopcock H opened, which allows the material to run into the dish in B without removing the bottle. In this way many liters of the solvent may be evaporated in any one dish, and the total amount of extract obtained together. At the last the bottle B is removed, and the extract which is found in the dish is ready for further operations.

APPARATUS FOR EVAPORATING IN VACUO.

Many of the operations in the laboratory require the evaporation of the material in vacuo. Especially is this true where the recovery of organic matters in solution is desired, which are easily altered at a high temperature. The evaporation is effected by the apparatus represented in Fig. 14. W is a water bath or steam bath, in which is placed a stout copper hemisphere, B, with flat edges. This hemisphere, B, is connected by a gum gasket, C, with a bell-jar, G, and this bell-jar is connected by means of the stopper through the stopcock H, with the safety flask, A, and the vacuum pump connected with E. An indicator, I, shows the amount of vacuum. The liquid to be evaporated is placed in B, the pump connected with E is started, and when the air is exhausted to the proper degree the water bath is heated or steam is admit-

ted to it until the liquid begins to boil. By means of this apparatus in my laboratory we are able to carry on evaporation for any length of time with a vacuum of from 26 to 27 inches.

We have a somewhat larger one than this which we use for larger quantities of liquid, which is furnished with a regular condensing apparatus, such as is used with large vacuum pans. This apparatus has also given the very best results in practice.

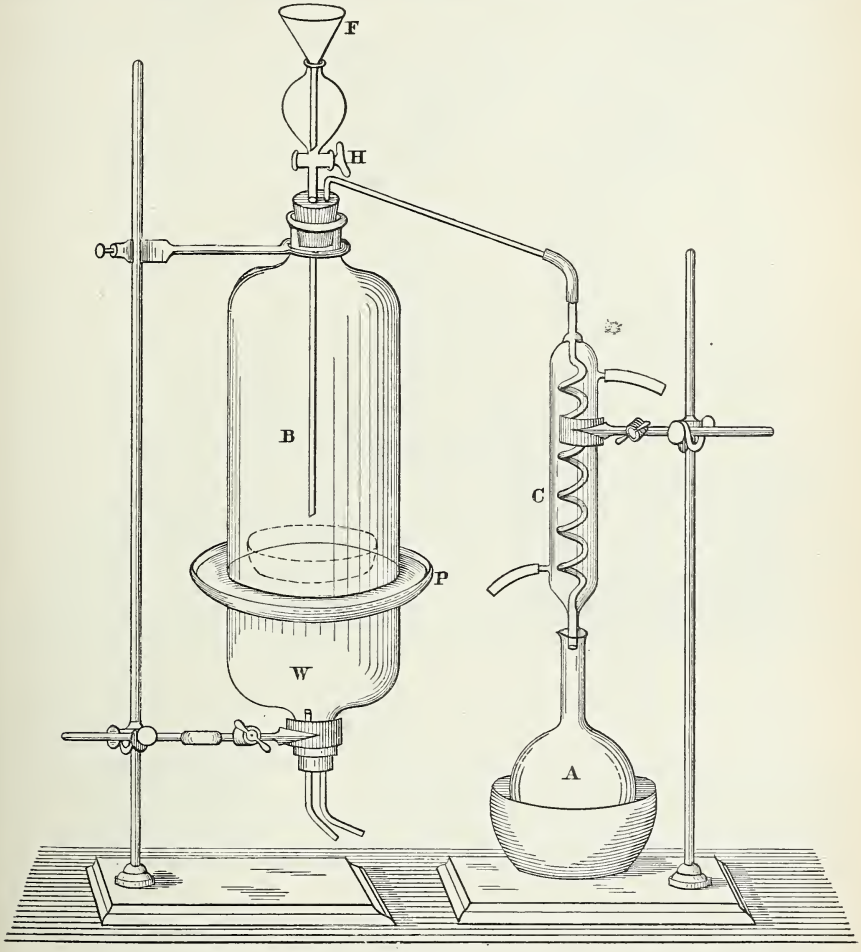


FIG. 13.

Where small quantities of liquid are to be evaporated the following device, shown also in Fig. 14, has been found to be successful. A large test tube, F, of strong glass is used. The material to be evaporated is placed in this test tube, and it is connected by means of a rubber tube, V, with the safety bottle A, and the exhaust pump connected with E. A small glass tube, *t*, drawn out to a fine point, extends, as shown in the figure, to the bottom of the test tube. This is furnished with a rubber tube and a clamp at K. This clamp can be set so as to admit a small stream of air through *t* to the bottom of the test tube. This air keeps the liquid to be evaporated in constant motion, and thus prevents bumping, and at the same time greatly aids the evaporation. The amount of air entering can be so regulated by the clamp K as not

to interfere with the vacuum. By means of this simple apparatus very small quantities of a liquor can be evaporated very rapidly to a very small bulk, and the substances sought are left in the tube ready for examination. We have found this simple form of apparatus to be especially valuable in the obtaining of vegetable extracts, such as sugars, etc., in a pure state and in a proper form of concentration for

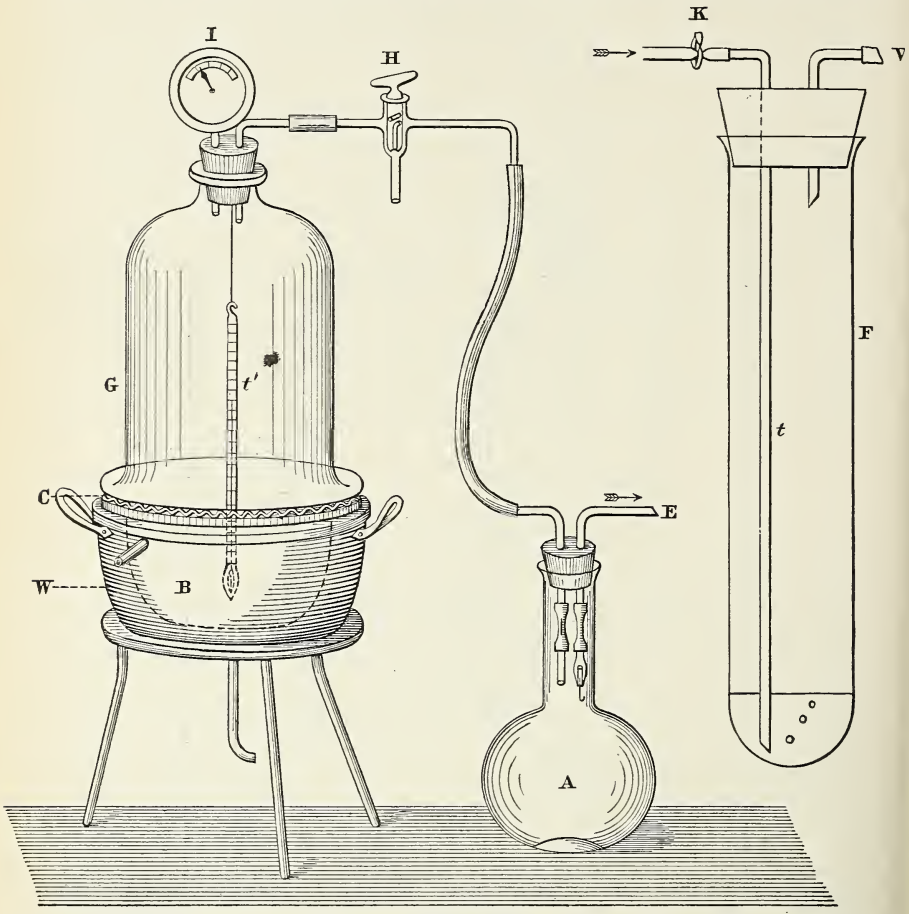


Fig. 14.

crystallization. I use in my laboratory, instead of a small Sprengl pump, a large vacuum pump connected with a reservoir in which a constant vacuum of about 26 inches is maintained. This reservoir connects with all the different desks in the laboratory, so that an apparatus of this kind can be used at any point in the laboratory at once by simply fitting up a test tube as described.

The apparatus just described has given such excellent results in use as to merit a more extended description. The smaller apparatus as used by me is illustrated in Fig. 15. A is the heavy test tube containing the liquid to be evaporated, and H is the supply beaker from which A is fed through C as the evaporation proceeds. A three-way stopcock, *a*, permits either the liquid in H to be drawn into the tube or air only, at the pleasure of the operator. In practice I have found it better to replace the three-way cock with a T-tube with two rubber connections carrying a screw clip. The quantity of liquid or air thus introduced can be exactly controlled. It is best to

establish a continuous feed from H of such volume as to maintain nearly a constant level in A until the liquid is all out of H. It is evident that A may be replaced by any shaped flask or tube capable of resisting the pressure of the air.

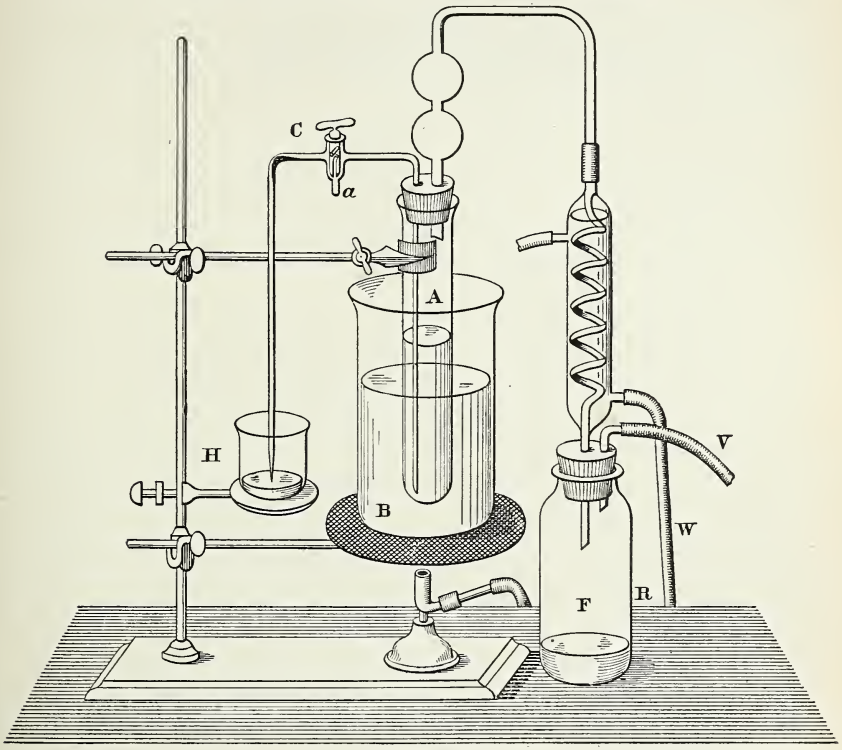


FIG. 15.

The two bulbs blown on the connecting tube between the condenser and A serve to prevent any loss of material from foaming or too violent ebullition. Foaming is very apt to occur if the feed from H be intermittent and a large quantity of liquid be drawn into A at one charge. F is a strong flask for receiving the water of condensation. W is connected with the water supply for keeping the condenser cool, and V leads to the vacuum pump. The water in the beaker B should be kept only a few degrees above the boiling point of the liquor in A. The stream of air admitted through *a* should be sufficient to prevent bumping and strong enough to hasten evaporation by carrying off the aqueous vapor.

Mr. Huston said that he had a paper by Dr. Stone, entering into the consideration of nitrogen-free extract; he would present it later on.

The president stated that the consideration of the recommendations made by the reporter was now in order, to be followed by any other recommendations which might be offered. The reporter would present his recommendations severally.

Mr. Caldwell said that he did not care to offer his first recommendation in the form of an amendment; it was rather a suggestion to the reporter that the method be tested during the year to ascertain its importance.

The second recommendation was in regard to the ether extract; it was proposed to either simply use the portion in which moisture had been determined as above, or dry 2 grams four hours.

Mr. Huston said that he thought the moisture and the ether extract could not be determined together with any degree of accuracy. A sample in which the extract dropped from 9 to 2 per cent on drying would not answer.

Mr. Caldwell said that the point made was very important. Was the association ready, however, to make the suggested change in the official method? If the association thought best, he was perfectly willing to make it, but it should be remembered that this was the official method by which the analyses were to be made during the year. The change was a radical one.

Mr. Huston said that, as he understood it, the analyst was to take 2 grams dried four hours or the sample in which the water had been determined. He did not see that these things were at all alike. He might be out of the way in his method of determining water, and perhaps heated it too long, but he had had cases in which it took over two hundred hours in a stream of hydrogen to get all the loss, and he was certain that in such a case one could not get ether extract; and if a water determination was to be made and all the volatile matter reduced to minimum weight before extraction, the variation would range from 5 per cent up to 80 per cent, but he did not believe that it would be possible to get out more than 80 per cent ether extract. He thought it might be desirable to omit the first clause: "Dry 2 grams of the substance four hours," and so on. He believed it would be a mistake to say that the ether extract could be made in the same sample that was used for the moisture.

Mr. Caldwell said that he understood it to be Mr. Huston's opinion that drying for four hours would not fully expel the moisture, and that the slight amount left would make a difference as compared with the result obtained by fully drying. Of course there was a very small quantity of moisture left after drying four hours, and his supposition had been that whether the drying was continued for four hours or for twelve hours the result would be practically the same as with ether.

Mr. Huston said that that was not his idea; the methods might work out that way in the end, but he thought that the water which was left had comparatively little to do in causing the trouble, and cut a comparatively small figure in the fat extractions, even in cases with water saturated ether worked forty-eight hours. The chief sources of trouble were the volatilization of some matter soluble in ether and what was called provisionally the change in the cell wall. If the association was not ready to leave out the four hours drying, that might stand, but as for the other matter—the sample used for getting the water—that was much worse than the four hours, and should not be inserted. Most men would not admit that a four hours' drying was sufficient to determine

the water. The fat extract in linseed meal would be worthless, and he thought that nothing ought to be inserted which would make the methods worse than at present.

Mr. Caldwell said that he would withdraw the recommendation.

Mr. Wiley said that, in his opinion, the object of a cattle-food analysis should be to determine as nearly as possible the quantity of a given substance present in the food. The use of anhydrous ether was recommended, and the object of the recommendation to dry the substance in hydrogen was that the water present in the sample should be removed so that the ether used for the extraction should remain anhydrous. If by this process there was really a diminution of the amount of substance extracted by the ether, and there evidently was, then was this additional substance due to the action of the water entering the ether on bodies soluble in water in the sample? If so, the analyst would get a portion, say, of carbohydrates. He believed that the minute portion of water which would enter ether through the sample was wholly insufficient to act on water-soluble bodies in the sample, and that the increase resulting from the use of ether was due solely to the extracting of bodies soluble in ether; these were more accessible to ether in the undried state. He thought that Mr. Huston's work showed conclusively that there was a loss of the very substance which it was desired to get by the previous drying, and nearly all would agree—his own experience upon the point was positive—that four hours' drying in hydrogen was wholly insufficient for estimating the volatile matter at the boiling point of water; the substance must be dried longer. Therefore the introduction here of this four hours' work would be, in his opinion, not only unnecessary but hurtful, and would not serve for the estimation of water. If the water was estimated there would be an enormous diminution of the amount of matter soluble in ether. Drying only four hours, less damage would be done, but a portion of the fatty bodies would certainly be rendered inaccessible to ether. He would like to see it recommended that the substance be dried four hours in hydrogen—making that specific; then strike out the *or*, as suggested by Mr. Huston, making it read, "in the sample in which the water has been determined;" and then recommend that it be also extracted in the air-dried substance. While conservative himself, and personally convinced that the four hours' drying was hurtful, he would not ask to have it stricken out without a further trial. He moved that the recommendation of the reporter be so amended as to direct that the ether extract shall be made with absolute ether on a substance dried four hours in ether at the boiling point of water, etc. The ether extract on the air-dried substance in the samples sent out to be also reported upon.

Mr. Woods said that there seemed to be two considerations in view in getting up the program, one being that of the methods which should govern the work, and the other the matter of testing the few samples sent out. If the proposed methods were to be applied only

to the samples received from the reporter, that would be one thing; it would be a wholly different thing used as a working scheme for the year. In his own work it was impossible, or impracticable, to carry dryings in coarse fodders to anything like the point at which they would cease losing weight. He thought that working schemes and schemes for experiments should be kept distinct, and that the recommendations of the reporter should not be adopted as the official method.

Mr. Caldwell said that he agreed with Mr. Woods, and had, therefore, said nothing about any change in the sample. He believed it would be well to keep the official method for the next year entirely distinct, and to make it as simple as possible, involving no more manipulation or drying than was necessary. Then the various changes desired might be added at the end.

Mr. Wiley said that he would withdraw his motion; he had not looked at the matter in the light now presented. He agreed with the last two speakers that it was better to adopt a method for general work, and afterward recommend such important methods as should be put forward for comparison. He moved that in the official method, under the head of "Moisture" (page 226), the water be determined by drying four hours in a current of hydrogen. Carried.

Mr. Anderson asked whether the hydrogen passed through the substance was previously heated.

Mr. Wiley said that the specific heat of hydrogen was so low that it was useless to heat it before passing through.

Mr. Huston said that it seemed to him important that in the official method some guide should be given as to the rate at which the hydrogen was to go through; he passed it through at the ordinary combustion rate.

The president said that no amendment of the method for pure ash was recommended.

Mr. Woods said that for practical working he would move to amend the method by striking out the part relating to determination of carbon dioxide.

The president stated the motion to be that all after the words "dry the whole at 110° and weigh," in the method for pure ash (page 226), be stricken out. Carried.

Mr. Woods said that in his experience it had proved to be simpler and more accurate to char after the evaporation at a low red heat than to dry at a temperature of 110°. He had rarely failed to find some organic matter present, however careful he had been in the first charring. He moved to further amend the method for pure ash by striking out the words, "dry the whole at 110°," and substituting in place thereof the words, *and heat to low redness until the ash becomes white.*

The amendment was agreed to, and, on motion, the method for determination of pure ash, as amended, was adopted.

At 12.30 p. m. a recess was taken.

AFTERNOON SESSION, FRIDAY.

The convention was called to order by the president at 2 p. m.

Mr. Wiley said that on the preceding day one point in the matter of butter analysis had been passed over. Mr. Knorr would call attention to the method of calculation for specific gravity instead of weighing.

Mr. Knorr said that his reason for undertaking the calculation referred to was that in determining the amount of water contained in the flask at the boiling temperature he had been unable to obtain concordant results, owing to the formation of very minute bubbles of vapor of which he could not get rid. He therefore thought it more accurate to calculate the weight of water at 100° in the flasks, which was done by a formula obtained from the tables of Landolt, and now placed upon the blackboard for the benefit of those present who had not the tables. (See page 197 in methods).

The president said that he had been asked at what point in the order of business resolutions should be submitted, and he would state that these would properly come in under the seventh order of business as set forth in the programme which had been agreed to, namely, business meeting, election of officers, etc. General resolutions could be handed to the secretary at any time, to be taken up when reached in the regular order.

He wished also to state his own pleasure and that of the association at seeing present so many chemists who were not members of the association. In regard to their standing, he had referred to the constitution, which contained the following clause:

> All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall have no vote in the association.

Basing his decision upon this clause, he would hold that such chemists were entitled to make and discuss motions, and otherwise take part in the proceedings of the convention, with the single exception that they could not vote.

The continuation of the subject of cattle foods was now in order.

Mr. Caldwell said that the next matter to be taken up was that of the ether extract. The direction was to dry 2 to 4 grams of the substance in a current of dry hydrogen at the boiling point of water. It would then, as he understood, read as follows:

> Exhaust the residue from the determination of moisture, or another portion dried in the same manner, with anhydrous and alcohol free ether until extraction is found by test to be complete.

He moved that the method as so modified be made the official method for the ensuing year. Seconded.

Mr. Wiley inquired whether, in the opinion of the reporter, it would be practicable to fix a definite number of hours. Some substances would continue indefinitely to give up material to ether, and under the

rule proposed the extraction would never come to an end. Uniformity and applicability were to be sought, and if there could be substituted a definite number of hours as the time in which the extraction should take place, the results would, he believed, be more satisfactory. However, he had not done enough work upon food stuffs to know all about the matter, and would be glad to have the reporter's opinion and that of others who had large experience in that line.

Mr. Caldwell said that the suggestion was a very good one, and it was for that reason that he had called the attention of the association to the latter part of the process; it was a question whether that should remain unchanged. He was not sufficiently experienced in that regard, nor had he watched the work of his assistants enough to be able to give an opinion, and as to whether it would now be best to fix any time, or to put in a time certainly safe, say eight hours or four hours, he was uncertain.

Mr. Farrington said that it seemed absolutely necessary that some such time should be adopted, but in extracting with ether the fineness of the sample should also be taken into consideration.

Mr. Huston said that in his extractions, except in one or two cases which would be considered entirely outside the range of ordinary work, fully 90 per cent of the extract was yielded in the first twenty-four hours, and in many cases much more than 90 per cent. He believed that the remaining extract was not a real fat. Of course, in the quantity he used, 2 grams, it was very small; but it seemed to have none of the properties of the real fat. The scheme which he believed was first described by Mr. Scovell, of leaving the extractor stoppered over night and starting it again on the following morning, was certainly ample for the purpose. He was not in a position to say whether the maceration in a Soxhlet apparatus over night removed more fat. It certainly removed considerable coloring matter; but he thought that in his own work the first twenty-four hours gave all the fat.

Mr. Caldwell said that he had understood Mr. Wiley to refer to the drying of the ether extract.

Mr. Wiley said that he had referred to the time of extraction.

Mr. Caldwell said that he had read an account of the results obtained in a large number of experiments made in the Missouri Station, where some sixty or perhaps one hundred tests of ether extraction were made, the result of which showed that the extraction was complete at the end of thirteen or fifteen hours.

Mr. Atwater asked with what substances the tests mentioned were made.

Mr. Caldwell said that they were made with the three samples sent out.

Mr. Wiley moved that the recommendation made by the reporter be so amended as to direct the extraction for sixteen hours with absolute ether. Seconded.

Mr. Huston asked whether the ether was to be left in contact with the material over night.

Mr. Wiley said that could be done when a Soxhlet tube was used, but some did not use that apparatus. He thought that the direction should be simply to extract for sixteen hours.

Mr. Atwater said that it could be done without a Soxhlet tube; it could be done with a Johnston.

The president stated the motion to be that the recommendation of the reporter be so amended as to require definitely exhaustion with anhydrous and alcohol-free ether for sixteen hours, instead of "until extraction is found by test to be complete."

Mr. Patterson said that stopping over night had been spoken of, and he wished to know whether a continuous extraction for the time specified would be prohibited.

The president said that it would not.

The amendment was agreed to, and on motion, the method for determining ether extract, as amended, was adopted.

Mr. Caldwell said that under the head of "Crude Protein" (page 226), he recommended that all after the word "protein," occurring in the second line of the paragraph, be stricken out as unnecessary. He believed that the matter of the standard was to be provided for in the report which was to come before the association.

The recommendation was adopted.

Mr. Anderson asked whether any time was fixed for the drying after extraction with ether; the direction was to dry to constant weight.

The president said that no time had been fixed.

On motion, the method for determination of crude protein, as amended, was adopted.

Mr. Caldwell moved that the method for determining albuminoid nitrogen remain the same as it was last year (pages 226,227). Seconded.

Mr. Patterson asked whether there was any objection to drying the copper residue before digesting with the Kjeldahl process. When it was put in wet he had trouble with frothing; it was just as convenient to dry as not to dry in his work.

Mr. Caldwell said that he could see no objection; there seemed to be no possible escape of nitrogen. The direction was inserted merely as a matter of convenience.

The president suggested that the words "without drying" might be stricken out.

Mr. Caldwell moved that the amendment suggested by the president be made. The amendment was agreed to, and on motion the method for determining albuminoid nitrogen as amended was adopted.

Mr. Caldwell moved that in the method for determination of crude fiber (page 227), the second, third, and fourth paragraphs (being all that portion of the method beginning with the words, "while this boiling is going on," and ending with the name "W. P. Cutter," in parenthesis) be stricken out. Carried.

Mr. Caldwell moved that the first part of the fifth paragraph be amended so as to read as follows: *Filter, wash thoroughly with boiling water*, etc. Carried.

Mr. Caldwell moved that the words, "and also with the air blast, both tubes," in the fourth line of the first paragraph be stricken out and the words *the tube* substituted in place thereof. Carried.

Mr. Farrington asked whether there would be no mention of the air blast.

Mr. Caldwell said that the words *and the blast of air* might be put in.

Mr. Woods said that it would be a good thing to insert that.

Mr. Caldwell moved that in the sixth line of the first paragraph the words *a blast of air may serve* be substituted for the words "the blast of air serves." Carried.

Mr. Caldwell said that he had nothing further to propose on the subject of crude fiber. It was questionable whether the strength of the acid should be changed; he did not think the association was prepared for that.

Mr. Woods inquired why it was necessary to wash with alcohol and ether in operating on a substance that had already been thoroughly extracted with ether.

Mr. Caldwell said that it greatly facilitated the drying of the substance.

Mr. Woods said that in the cases he had tried side by side he found no gain in the drying, even in a substance where he had 0.6 of a gram of crude fiber.

Mr. Caldwell moved that the words "wash then with alcohol, finally with ether," in the sixth line of the fifth paragraph, be stricken out. Seconded.

Mr. Atwater said that the motion seemed appropriate; he did not know that any one could say with certainty that nothing would come from the further extraction, but, as Mr. Woods had said, it had been tried in their own laboratory and no further extract was obtained.

Mr. Farrington said that he thought it was very well to wash with absolute alcohol and ether, and that it would not be well to discontinue that washing until the association had some figures upon it.

Mr. McDonnell said that the washing with alcohol seemed desirable; in some cases it would remove some of the coloring matter which was still present. He did not think that the washing with ether was of advantage; it certainly was not so far as drying was concerned.

Mr. Woods said that he did not know but that something would be extracted in some cases. In the case of such a coarse fodder as hay nothing was extracted by the alcohol after extraction by ether.

Mr. Anderson said that he had lately been working with green corn, and had observed that in washing with alcohol after extraction the alcohol was in every case colored.

Mr. Caldwell said that the policy of the association had been some-

what changed, and it was now desired to get a practical working method which would be sufficiently accurate for the purpose, although perhaps not scientifically accurate. This plan had been followed beginning with the method for moisture. The last statement seemed to make the matter rather doubtful. He agreed with Mr. Atwater that it was difficult to understand what the further extraction would be.

Mr. McDonnell said that in the cases he had referred to, where the color was extracted, no thorough extraction with ether had been made previously.

The amendment was agreed to, and on motion, the method for determining crude fiber, as amended, was adopted.

Mr. Caldwell said that the last paragraph in the method for cattle foods (page 228) was simply a request that the chemists should pursue an investigation which the larger part of the experience during the past year had certainly proved to be unprofitable. He moved that the paragraph in question be stricken out.

Mr. Huston said that he was so well pleased with the petroleum that he would be glad to have the association give further consideration to the matter. He agreed that it ought not to be included as a part of the official method for the ensuing year, but wished that the request to try it might be continued, believing that it might yield good results.

Mr. Caldwell said that several suggestions were to be made in regard to the conduct of the comparative work during the coming year, and the matter now referred to might be brought in among those. He merely wished to take it out of the official method.

The motion was carried.

Mr. Caldwell said that perhaps it would be necessary to go back to the subject of ash and strike out the word "pure," as the ash was not now pure.

The president said that unless objection was made the word might be stricken out.

Mr. Caldwell said that Mr. Woods had asked whether it was necessary to retain the paragraph next to the last one in the method. It was at most a mere matter of advice, and hardly amounted to that. He moved that the paragraph be stricken out. Carried.

Mr. Caldwell said that it remained to consider suggestions for comparative work in addition to comparing the official method. He would first suggest a very much more thorough sampling of the material before it should be sent out by the reporter to be tested. He moved that for the purpose of sampling, the whole mass of ground substance be put in a square box, not to be more than two-thirds filled, and which should be provided with blades of wood stretched from side to side across a portion of the area, the box to be caused to revolve for a number of hours daily, in order to ascertain whether the discrepancies observed are due to differences in analyses or to want of thorough mixture. Carried.

Mr. Caldwell said that his next motion, made upon the suggestion of Mr. Wiley, was that the extraction by anhydrous ether of the air-dried substances as sent out be made one of the requirements in the experimental work of the ensuing year. Seconded.

Mr. Burney said that Mr. Huston had stated in his paper read this morning that he had taken absolute ether, added to it the amount of alcohol contained in Squibb's ether, and had then extracted the feeding stuff with that ether, and had found an increase in the amount of extracted matter. He would ask Mr. Huston whether he had examined that extracted matter for the purpose of determining whether it was organic or inorganic; and, if so, with what results?

Mr. Huston replied that no further examination of the material was made. He considered that in everything except oil meal the quantities were too small to afford good results, and he was nearly out of material, having but three or four grams left. He determined no ash in those.

The president stated that the requirement under consideration was not to be understood as a part of the official method, but as one to be observed in testing the samples sent out during the year.

The motion was carried.

Mr. Caldwell moved that the purification of the ether extract by causing it to pass through animal charcoal, as suggested by Mr. Patterson, be tested, and said that he should like to see that suggestion applied to both extracts, that of the dried substance and that of the substance taken in its natural condition. The chemists might not be able to do so much, but it was offered as something to be done by those who had sufficient time. Carried.

Mr. Caldwell said that he had no further suggestions to make in regard to changes in methods of working. He would like to say something in reference to a somewhat different manner of getting the work done, if that would now be considered in order.

The president said that the matter was in order.

Mr. Caldwell said that, as stated in his report, it was evident that many of the chemists had but little time to spare for the experimental work, and it seemed that some of the work which had been done in that line was hardly worth doing. He thought that it might be well to confine the work to that constituent which had given the most trouble, namely, the ether extract. The samples should be sent out as early as possible, and only to chemists interested in the subject, and who would put experienced men upon the work. In this regard he had undergone a change of heart. Last year he had stated that the work might be useful as affording good practice for the younger analysts in the experiment stations, but now he did not consider this to be the purpose of the work of the association. What the association wanted was a method known to be, in accustomed hands, reliable, of which it could be said to the young men as they came in, This method is reliable, and

you will have to get good results by it. He would suggest that only the chemists of stations more particularly interested be asked to undertake the work, for if ten chemists could be given one line of work and ten others another line, the results would perhaps be better; and the reporter should confine his requirements for the experimental work, and even for the other work at first, to one subject, that of the ether extract on the carefully sampled portion. The results should be sent in not later than, say, January 1, giving the reporter an opportunity to put them in order, see how they came out, and then request a further examination if they did not come out well, showing that the trouble was in the sampling, or that some of the work had been done by inexperienced chemists. At any rate, the work on cattle food for the year, both by the official method and upon the new matters suggested, should be confined to a smaller number of chemists, and those undertaking it should be requested to put it in the hands of those only who were experienced in fodder analysis, limiting the investigation at first to the ether extract, which was the most troublesome constituent, and leaving it optional with the chemist to do the rest of the work. He threw this out as a mere suggestion, and would like to see whether it met with the approval of the association.

The president said that a vote could be taken upon the suggestion to the reporter; it would have to be put in the form of a motion.

Mr. Stubbs moved that the action suggested by Mr. Caldwell be recommended to the reporter for the coming year. Carried.

Mr. Houston said that in the preparation of the sample the substance was directed to be ground until all of it would pass through a sieve with thirty-six meshes to the linear inch. He believed than one of the chief sources of difference in cattle food analyses was to be found in the fact that so-called thirty-six-mesh sieves varied greatly, there being no standard size for the wire. The sieve specified in the method for phosphoric acid was definitely described; the cross section for the space through which the material should pass was stated; but "thirty-five-mesh sieve" or "thirty-six-mesh sieve" could not be definitely understood, the meaning depending upon the freak of the gauze maker. He had a so-called twenty-three-mesh sieve which was finer than the thirty-six-mesh sieve.

Mr. Farrington said that the matter of the sieve was very important and he would move that the description of the sieve be made to apply to the diameter of the hole, expressed in millimeters.

Mr. Caldwell said that all the samples sent out were put through the same sieve, and it was stated on the blanks that no further change was necessary. He would correct the matter in the report, and it would not be necessary to put the question on Mr. Farrington's proposed motion. The diameter of the orifice had not been stated; it was 1 millimeter, the size of hole adopted by the experiment stations in Germany as practical after carefully considering the matter at their meeting.

Mr. McDonnell asked whether the hole decided upon by the German experiment station was a round one.

Mr. Caldwell said that he did not remember positively, but thought that it was.

Mr. Wiley said that it was a matter of great difference whether the hole was round or square, and he thought it important that the association should adopt a sieve having circular holes 1 millimeter in diameter.

Mr. Caldwell said that he would so prescribe.

Mr. Farrington offered the following resolution:

Resolved, That in the opinion of this association it is desirable to publish with the results expressing the percentage of dry matter in feeding stuffs a description of the process by which such results are obtained, or a reference that will give such description.

In support of the resolution he said that although it was known what to expect in making an estimation of dry matter in feeding stuffs, the chemists might be better able to form their opinions if they knew how the results reported were obtained in each case. Not every analysis referred to the official methods, and nothing was said as to how the dry matter was obtained, which it was important to know.

The resolution was adopted.

Mr. Cooke said that one matter which had come up in times past, and had several times been spoken of in the meetings of the association by Mr. Jenkins, had not yet, so far as he knew, been acted on by any of the reporters. He referred to the method of stating average results. The reporters brought in the figures of the different chemists and gave the arithmetical average of all those figures, thus giving as much weight to a wide result as to one very nearly correct. The final computations were almost always made by clerks who could just as well go into a longer calculation that would give figures representing a probable mean and the probably correct result. The method of least squares would give the correct result, but the mere arithmetical average would not.

In regard to the determination of moisture in cattle foods, as the samples were now sent out it was hardly possible to compare the results obtained by the analysts; this could be done if the samples were forwarded in glass, sealed, as were the samples sent out for determination of phosphoric acid and nitrogen, and then the results on ether extract could be taken for the crude fodder directly from the sample without, as was now the custom, transferring to dry matter, to which errors made in moisture are carried, making the results on the ether extract or the crude fiber appear wider on paper than they are in reality. He thought that if the samples could be sent out in such a way that they would not lose or gain in moisture the results would be brought more closely together, the comparison being that of figures obtained on the original substance instead of on dry matter.

Mr. Caldwell said that the idea advanced was a very good one. He moved that the reporter on cattle foods be requested to send out the samples in sealed glass vessels. Carried.

Mr. Atwater presented the following report on behalf of the committee appointed at the previous annual meeting, consisting of Messrs. Atwater, Caldwell, Jenkins, Jordan, and Wiley:

REPORT OF COMMITTEE ON WAYS AND MEANS FOR SECURING MORE THOROUGH CHEMICAL STUDY OF FOODS AND FEEDING STUFFS.

At the meeting of the Association of Official Agricultural Chemists at Washington, September 10–12, 1889, it was voted "that a committee be appointed to consider and report upon ways and means for securing more thorough chemical study of foods and feeding stuffs, with the purpose of obtaining such information as will aid in the improvement of methods of analysis and in the more satisfactory estimation of nutritive values." The committee respectfully report as follows:

The object sought in the appointment of this committee is more fully expressed in the discussion at the meeting, including especially that which accompanied the resolution referred to.

This evinced a very general feeling that our present methods of analysis of foods and feeding stuffs are unsatisfactory. It was urged by a number of the members that the common grouping of proximate ingredients does not correspond accurately enough with either their chemical or their physiological relations; that the current methods of determination, in the hands of different analysts, give varying results; and that even if uniform results were obtained, they would not show accurately the nutritive values which it is the object of analyses to learn. It was still further urged that the development of the experiment station system and the great increase in the amount and importance of the analytical work done emphasized the demand at the same time that it improved the opportunity for improvement, and that this improvement must be sought in abstract and thorough chemical study of the substances we are dealing with.

The urgent need of perfecting our analytical methods was also insisted upon by the committee on analysis of cattle foods, and was enforced by their report of analyses made of the same material by different experiment stations. The amounts of ether extract in the same sample of hay reported by sixteen stations ranged from 2.66 to 7.10 per cent, reckoned upon dry substance. The average was 4.78, and the mean 4.88 per cent. The difference between the highest and lowest per cent was 4.44, and this difference expressed in per cent of the average of all the results was 96.79. The differences in other ingredients were smaller, but in the crude protein, of which the average was 12.63, the highest per cent reported differed from the lowest by 3.06, which was 24.23 per cent of the average.*

The ideas thus expressed at the meeting are current among agricultural chemists in this country and in Europe. The feeling is becoming more and more general that a reform in our methods of analysis is needed, and that this must be based upon the more thorough study of the materials to be analyzed. One phase is summarized in the words of two members of the association at the meeting referred to. One remarked that the "analyses must be governed by the chemical nature and structure of the bodies dealt with; and a thorough chemical knowledge of the proximate ingredients of our animal and vegetable products is a crying need." The other, in urging the importance of more careful investigation in this direction, said: "The key note to the future success of the work of the experiment station and of the analytical chemists has been struck in calling attention to the absolute necessity of sooner or later getting underneath what lies upon the surface."

The importance of this matter has been recognized by the Department of Agriculture. The report of the Director of the Office of Experiment Stations, which makes a part of the report of the Secretary of Agriculture for 1889, contains the following:

* See, however, statements by Mr. W. W. Cooke, of the Vermont experiment station, page 128.

"A great deal of experimenting has been done and is now in progress to discover the nutritive values of food materials, the laws of nutrition, and their proper application. Experimental science has advanced to the stage in which more thorough inquiry into the fundamental principles of these subjects is necessary. Many analyses of feeding stuffs are being made by the stations, and standards for rations for domestic animals have been proposed and are widely used; but the results of actual feeding tests do not always agree with those obtained by analysis and recommended in feeding standards. While analyses of feeding stuffs by the methods now current have been and are of the greatest service, especially when combined with results of experiments upon digestibility and other physiological research, it is universally recognized by agricultural chemists that chemical analysis alone gives a very inadequate idea of the true nutritive value of a feeding stuff. The late advances in physiological chemistry all point to the possibility of getting such knowledge as will show feeding values with reasonable accuracy. One thing now especially needed is a thorough study of the chemistry of vegetable and animal products used for food. For this purpose it is essential to make more accurate separations of the proximate compounds and investigate them individually with reference to their molecular constitution and their potential energy. This means the most accurate, profound, and detailed research in analytical, organic, and physiological chemistry. It will require much labor and that of the highest scientific order, but neither its magnitude, its difficulty, nor its cost should prevent its being undertaken and carried to successful issue. The interests of the agriculture of the country as well as of scientific advancement are too great to permit its neglect."

On page 248 of vol. 1 of the Experiment Station Record the same idea is expressed in the following language:

"It is important, indeed indispensable, that we have more thorough knowledge of the chemical constitution of the materials used for feeding stuffs. The studies need to be prosecuted in such ways as to determine, for each species of plants, and for the different parts of the same plant, the kinds of proximate ingredients, the amount of each ingredient, and its molecular constitution, its digestibility, and its fuel value as measured by its potential energy."

We make analyses of foods and feeding stuffs to determine their nutritive values. To plan proper methods of analysis, we have then to consider on the one hand the composition, solubilities, and other chemical properties of the proximate ingredients, and on the other their physiological characters, their digestibility, and their functions in nutrition.

At present we determine, or assume that we determine, one group, which we call protein, by multiplying the total nitrogen by 6.25; a second, which we call fats or crude fats, by extracting with ether; a third, which we call fiber or crude fiber, by extracting with dilute acid and alkali; a fourth, which we call ash, by incineration, and a fifth, which we call nitrogen-free extract, by subtracting the sum of the first four from the total water-free substance, which last we get by subtracting from the whole weight the weight of water as determined by more or less accurate dryings.

We know that the proximate ingredients which we thus roughly class as belonging to each of the four groups, protein, fats, nitrogen-free extract, and fiber, differ in different plants, and in different parts and in different periods of growth of the same plant, in respect to number, chemical properties, and nutritive values; that there are compounds even in our common foods and feeding stuffs which do not properly belong in the groups in which we class them; that the figure found for each group in any given plant or part of a plant (and the same is true, although in less degree, in animal substances) by our current methods of analysis is not entirely correct even with the best possible work in the laboratory; that in the hands of different manipulators the results are widely divergent; and that if our analytical results were perfectly accurate in themselves, they would not even then give us an exact measure of what we really want to learn, namely, the nutritive values of the materials analyzed. In short, we know perfectly well that our present methods of analysis are chemically and

physiologically imperfect. The results do not agree with practical experience, and we do not even agree among ourselves in the analyses we make.

This is of course a one-sided statement. In a sense it is exaggerated. A layman might infer from it that chemical analysis is an entirely unreliable means of estimating nutritive values. That would be unwarranted. The truth is, simply, that we are in the earlier stage of the development of our science, and that our methods are still crude. They have done and are doing service that is invaluable, but the time has come when greater accuracy is needed.

We represent the science of the country as related to its most important material interest. It is our office to pronounce upon the character of the materials we study and to advise people of their values and proper use. What are we going to do about it?

Evidently the first thing is to consider what we are dealing with. What, then, are the principal proximate ingredients of our more common feeding stuffs and food materials, and what are their properties as viewed from our standpoint?

In vegetable materials, by our present methods, we determine, or assume that we determine, one group, which we call protein, by multiplying the total nitrogen by 6.25; a second, which we call fats or crude fats, by extracting with ether; a third, which we call fiber or crude fiber, by extracting with dilute acid and alkali; a fourth, which we call ash, by incineration; and a fifth, which we call carbohydrates or nitrogen-free extract, by subtracting the sum of the first four from the total water-free substance, which last we get by subtracting from the whole weight the weight of water, as determined by more or less accurate dryings. In animal products used for food we have no crude fiber and the quantities of carbohydrates are generally so small, except in milk and its products, that we neglect them.

Protein.—This term is applied to a large number of materials which differ very widely in chemical and physiological properties. Even the terminology is in great confusion. We may here designate them proteids and non-proteids.

The proteids include the albuminoids, which are abundant in both vegetable and animal materials, and the so-called gelatinoids, which are especially characteristic of the connective tissues of animals. The vegetable albuminoids are very imperfectly understood. They are numerous and difficult of separation and are more or less readily transformed into one another. The per cent of nitrogen, which should be 16 to make the ordinary factor 6.25 correct, varies considerably, not only in different classes of albuminoids, but in those of the same class from different species of plants, and if the results obtained by different investigators are to be relied on, in those of the same class from different plants of the same species. With the animal albuminoids that chiefly concern us the case is somewhat simpler. They appear to be less in number, those which we group together are perhaps more nearly alike in chemical constitution, and they change less with the growth and development of the organism and in the keeping and handling in the laboratory. Generally speaking the nitrogen factor, 6.25, is not far out of the way for them. Still we must learn much from organic chemistry and histology before we can know how to separate and determine them and judge of their nutritive values with accuracy. The same is true of the gelatinoids, of which really but little is definitely known.

The non-proteid nitrogenous compounds include those to which the term amides is often applied, and which occur chiefly in plants; those which are frequently grouped with kreatin and are more characteristic of animal substances; and others, such as the lecithins, alkaloids, and nitrogenous glucosides, which occur to greater or less extent in either vegetable or animal materials or in both. They are widely divergent in chemical composition, and while some of them have a high nutritive value, others, including many with the highest percentages of nitrogen, neither form tissue nor yield energy in the body. At present there is no satisfactory way of determining them. Even the methods for "non-albuminoid" nitrogen in vegetable substances do not stand the test of critical experience. All of them demand further investigation.

It is perfectly clear then that the practice of determining the total nitrogen, multiplying it by 6.25, calling the product protein, and using it as a measure of the nutritive value of the nitrogenous ingredients, is a very rough and inaccurate way of doing things.

Fats—Ether extract.—The case with the so-called crude fat is no better. In such animal substances as muscular or connective tissue, milk and products from it, the ether extract, if obtained by proper manipulation, contains the fatty bodies and little else. But the compounds we extract from vegetable products and denominate as crude fat, ether extract, or for short, fats, are very diverse, nor are we at all sure what proportion of them we extract by our ordinary methods. We have to deal not only with the true fats, *i. e.*, glycerides of the fatty acids, and the fatty acids themselves which may be properly classed with the fats in estimating nutritive values, but also with a great variety of other compounds of widely differing constitution, and of whose functions and value in nutrition but little is known. Among them are vegetable acids other than the fatty acids, substituted glycerides including the various modifications of lecithin, waxes, alkaloids, cholesterin, hydrocarbons, and chlorophyls. Of these the lecithins appear to have a special value in nutrition, while some of the alkaloids are poisons.

If the substance to be analyzed is finely ground, free from water, and in otherwise normal condition and the cell structure allows easy extraction, we may in general expect that absolute ether, properly applied, will take out the whole of the true fats and fatty acids, and more or less of the other acids, lecithins, wax, chlorophyl, cholesterin, alkaloids, and solid hydrocarbons, and that more or less of the compounds other than true fats and fatty acids will remain undissolved. If the ether contains alcohol the extract may be expected to contain more of the other compounds. If water is present the extract may be, that is to say, in numerous observations it has been, apparently larger; but we do not know yet exactly what compounds are affected by the presence of alcohol or water, or to what extent.

It is well established that when vegetable products are heated in air as is done in drying, less ether extract is obtained. The theory is that fats are oxidized and rendered insoluble in ether. But what the specific compounds are and what chemical changes they undergo, we do not know. The amount of decrease in solubility is in some cases far greater than would be easily explained by the oxidation of linoleic acid. Are not other compounds affected, and do they not undergo more or less change on standing or in drying at ordinary temperatures? Such is familiarly the case with drying oils. May it not be so in the substances we have to analyze? And do not changes in the cell walls and incrusting materials, in standing and heating, have much to do in preventing substances of themselves soluble from being dissolved?

Incidentally these considerations suggest numerous queries. In drying in hydrogen are we always sure that the hydrogen we use is entirely free from oxygen? How much difference is there between the extract by absolute ether and by the ordinary ether we buy for pure ether? What of the effect of fineness of grinding and time of extraction upon the amount and composition of the extract? What difference does it make whether we use the fresh substance or that which has been standing in the laboratory or elsewhere for a long time?

At the last meeting of this association a member (Professor Scovell) reported a case in which he had obtained with absolute ether from hay 3.03 per cent of extract. By letting the extracted material stand one night with absolute ether, and extracting again the next morning, a larger result was obtained. With Squibb's ether, supposed to be anhydrous, but not alcohol-free, a much larger extract was obtained. Apparently the chlorophyl was more fully extracted by the use of Squibb's ether.

In inorganic analysis we have constantly to do with cases in which the solubility of a compound in a given reagent is materially affected by other compounds. Have we sufficiently considered the importance of analogous reactions in organic analysis?

For instance, some of the alkaloids are soluble in ether. Some are themselves insoluble in ether, but when associated with other compounds in vegetable or animal substances are extracted by ether in the ordinary process of fat determination. It is very likely the fats or fatty acids decide the solution; in other words, in the presence of neutral fats or fatty acids, alkaloids may be dissolved by ether which in their absence would not be dissolved.

Among the substances which cause trouble in fat determinations are the lecithins, which are partially soluble in ether. In the ordinary bean, of the total crude ether extract obtained by treating with alcohol, evaporating and treating the residue with ether, about 30 per cent has been found by Mr. W. Maxwell to consist of lecithins and 6 per cent cholesterin and 5 per cent solid hydrocarbons, which makes over 40 per cent of the whole crude extract to be other material than neutral fats. The following figures, which were kindly supplied by Mr. Maxwell, illustrate the quantities of materials other than fats which have been found in the seeds of the plants named. They help to understand why the amounts of ether extract obtained by different analysts are so variable.

Proportions of lecithins, cholesterin, etc., in one hundred parts of "crude fat" (ether and alcohol-ether extract) of seeds.

	Lecithins.	Cholesterin.	Hydrocarbons.	Fats and undetermined.
Bean*	29.5	6.0	5.0	59.5
Pea	†35.1	‡3.0	(§)	61.9
Horse bean	†47.8	‡2.0	(§)	50.2
Vetch	†28.0	‡4.0	(§)	68.0
Cotton (upland)	2.3	(§)	(§)	97.7
Maize	3.3	(§)	(§)	96.7

*Average of analyses by W. Maxwell.
†Average of results by Maxwell and by Jacobsen. Later results by Maxwell, not yet published, indicate that these figures are too small.
‡Average of results by Maxwell.
§Undetermined. Analyses by Wiley and Maxwell.

Among the numerous illustrations of the value of special studies in these directions may be cited the investigations by Stellwag,* who has studied the extracts obtained with ether and with "*benzin*" (the lighter hydrocarbons of petroleum?) from hay, seeds of cereals and legumes, bran, oil cakes, etc. He finds in the ether extract from hay about 23.7 per cent of neutral fats, 37.3 per cent of free fatty acids, and only traces of lecithins. In the grain of barley and oats and bran of wheat and rye the free fatty acids ranged from 14 to 35.4 per cent and the lecithin from 2.1 to 4.3 per cent. In the seeds of pea, vetch, and horse bean the percentages of lecithin were from 21.3 to 27.4; in cotton-seed cake the lecithin made 4.4 and in potatoes 3.1 per cent of the total ether extract. In the "*benzin*" extract the percentages of lecithin were in general much smaller. He considers "petroleum ether" of low boiling point a more proper solvent for fats than ether, because it dissolves less of the materials not fat, such as wax (bees'-wax) and numerous organic and mineral acids.

But perhaps the chief outcome of this, as of other valuable investigations, is to bring into clearer light the need of further and more detailed study of the subject.

It may be that such means as the case of animal charcoal for the purification of ether extract from non-fatty substances in the manner lately suggested by one of our fellow chemists† may prove useful. But it is clear that what we need to know first is the nature of the substances with which we have to do.

*Die Zusammensetzung der Futtermittelfette. Landw. Vers. Stationen, 37, 1890, 135.

†H. J. Patterson. Am. Chem. Jour., 12, 261.

The nutritive values of the materials which are more properly grouped as fats, *i.e.*, the glycerides of the fatty acids and the fatty acids themselves, are pretty well understood, though further investigation of the molecular constitution of some and of the potential energy of all is needed. The fact that lecithins seem to be readily assimilated by animals, that they are important constituents of brain and nerve tissues, and that on decomposition they yield fatty acids with large potential energy, all indicate for them a high nutritive value. The waxes are still imperfectly understood, but from what is known of their constitution it would seem that in so far as they are digestible their nutritive values must approximate those of the fats. Of the glucosides our present knowledge enables us to say but little. The same is true of the chlorophyls, cholesterin, the hydrocarbons, and the alkaloids.

According to the present outlook, therefore, it seems probable that although the waxes and perhaps the lecithins may be classed with the fats in estimations of nutritive values, a separate classification of some or all of the others will be necessary; and it is clear that a more definite knowledge of the chemical constitution of all the materials other than the neutral fats and fatty acids is indispensable to any correct estimate of their values for nutriment.

Carbohydrates.—The need of better understanding of these is hardly less pressing than is the case with the fats or protein compounds.

The ordinary classification of carbohydrates as glucoses, saccharoses, and amyloses will hardly suffice for the purposes of analysis or for the determination of nutritive values. For analysis a more desirable grouping will probably be based upon solubilities. We may perhaps distinguish between (1) those soluble in water, (2) those which are rendered soluble by digestive (diastatic) ferments, (3) those which are not so dissolved, but are dissolved by dilute acid or alkali, and (4) those which are not dissolved by either of the agencies named.

The first class will very likely include the glucoses, saccharoses, and, of the amyloses, the dextrines, galactans, dextrans, lævulans, and perhaps inulin, and others. The second will naturally consist of the starches and allied compounds, including (*a*) amorphous starch, which when suspended in water at 45° or thereabout is acted upon by ferments; (*b*) granulose starch, acted upon by ferments after gelatinizing by treatment with water at 100°; (*c*) cellulose starch, acted upon by ferments after gelatinizing by treatment with water or steam under pressure of two or three atmospheres. The third will include paragalactans and the substance which yields xylose on treating with dilute alkali (gums) and allied bodies. The fourth will include the celluloses and allied compounds.*

The place or places into which investigation will bring the pectins, mucilages, and other less understood compounds it is, of course, impossible to predict. For that matter this tentative grouping is suggested simply to illustrate what needs to be done.

It is essential to study carefully the carbohydrates which occur in different plants, in different parts of plants, and at different periods of growth and to learn their behavior with solvents and their methods of separation. It is also important to learn more about their digestibility and the ways in which they are utilized in the body. Much of the information must be gained by the methods of vegetable physiology and histology rather than by purely chemical methods.

Of the nutritive values of some of the carbohydrates, especially those which are soluble in water or are rendered soluble by the diastatic ferments, we have some definite knowledge. For instance, the sugars may be reckoned as completely digestible and the potential energy of a number of them has already been determined and others are being studied. The problem here is comparatively simple. With those that are not dissolved by either water or the digestive ferments the case is somewhat

* The classification here suggested is for the most part as has been proposed by Mr. W. Maxwell, but not yet published in detail.

more complicated, but it is to be hoped that research of the kinds now being carried on by several chemists in this country and in Europe will bring before many years much of the definite information which is needed.

As regards the celluloses we are still in doubt. The questions as to how they are digested by the agency of bacteria or of enzymes; what are the products of their fermentation, *i. e.*, how much is marsh gas, how much consists of acids of little or no nutritive value, and how much of substances akin to glucoses; to what extent those products are assimilated, their potential energy made available, and their service in forming fat or protecting protein from consumption is effective—all these problems still await satisfactory solution. Until they are solved the nutritive values of the celluloses must remain in doubt. It seems probable, however, that our present method of grouping these compounds will be followed for some time to come.

It is to be noted, with regard to compounds belonging to each of the above classes, that in many instances, especially with vegetable materials, the solubility of the ingredients in laboratory reagents, their digestibility in laboratory experiments and in the animal's body, and their nutritive effect are dependent upon the ways in which they are held in the vegetable tissues, *e. g.*, the nature of the cell walls or incrusting substances. Of these things ordinary chemical analysis tells us little or nothing, and we must look to the vegetable histologist to find out about them for us. Meanwhile in ignoring them we commit more or less serious error.

In providing for a proper classification of proximate compounds it will be necessary to study some of the less known substances for which we have as yet no fixed place, such as, for instance, the alkaloids and pigments. The effect of mechanical condition upon solubility and nutritive values, as in the case of cellulose, which has been found to be more digestible in young than in older plants, and likewise more digestible in plants grown in rich than in those grown on poorer soil, demands investigation.

The results of such research as has been above indicated will doubtless lead not only to changes in the general groupings and methods of analysis, but also to special groupings and methods of analysis for different classes of vegetable and animal foods and feeding stuffs.

It is hardly to be expected, for instance, that we shall always hold to the same grouping of compounds for grasses, cereal grains, leguminous plants and their seeds, root crops, milk, and meats. It is more probable that groupings for different classes of materials, with corresponding methods of analysis and of estimating the nutritive values, will prove both necessary and feasible.

To recapitulate, briefly: We have a partial, but only a partial, knowledge of the proximate ingredients of the vegetable and animal substances used as food for man and as feeding stuffs for domestic animals. We do not know exactly what ones are contained and in what proportions in different plants, in different parts of the same plant, and at different periods of development of the plant. We lack that information as to their chemical behavior which is needed to devise plans for their correct separation and determination, nor is our knowledge any more nearly adequate for estimating their digestibility and their nutritive values. The same is true, though to a less degree, of the compounds with which we have to do in animal substances. The classification which we are now using is crude and inaccurate from the standpoint of analytical, organic, and physiological chemistry. The results of our analyses are variable and at best inaccurate, and even if they were entirely accurate the estimates of nutritive values based upon them would often be very far from correct. The only way to get the information which is requisite for rational groupings of compounds, accurate analyses, and correct estimates of nutritive values is by the most thorough, painstaking research in analytical, organic, physical, and physiological chemistry.

The proper reform of our methods will evidently come as fast as does the chemical and physiological knowledge which must serve as the basis for it, and no faster. This means that the most abstract and profound study is necessary. Fortunately such study is engaging more and more the attention of chemists and vegetable physiologists.

From the chemical standpoint we need: First, such studies as will bring definite knowledge of the kinds and amounts of proximate compounds contained in each substance to be analyzed; that is to say, (1) in different plants, as grasses, grains, cereals, legumes, tubers, roots, etc.; (2) different parts of the same plant, as the stalk and seed of maize and wheat and the different parts of the wheat grain; (3) in the same plant at different periods of growth; (4) in animal substances. Second, studies of each compound regarding its behavior with reagents, *i. e.*, solubility, etc., its elementary composition, its molecular constitution; the changes it undergoes by the action of ferments; its digestibility; and its potential energy. Third, classifications of the compounds based upon the properties named. Fourth, improved methods for separation and estimation based upon the same properties. Fifth, as the outcome of all this, more correct methods of estimating the nutritive values.

This all means a vast amount of research, and that of the highest order. Its practical usefulness is as clear to the student as that of any experimental inquiry in which our Experiment Stations and other institutions for research are engaged.

But it is not easy to persuade the public at large of their immediate importance. It is not easy for Experiment Stations to secure the high order of talent and training that is needed, and devote the requisite labor to such inquiry.

Nevertheless the Stations can do something, and each investigation of value they make will help to the making of more. Organic and physiological chemists who have the opportunity and taste for research will find here a promising field, one which has the threefold advantage of newness, promise of results of the highest theoretical value, and assurance of practical usefulness.

Investigations in these lines have been already undertaken by the Department of Agriculture, and coöperation between it and the Experiment Stations and other institutions of research can not fail to be useful in the highest degree.

What is needed first of all, however, is the compilation of what is best known in these lines. When all that has been done is well put together we shall doubtless find that what has already accumulated is much greater and more helpful than we at present realize. The necessity of such compilation is all the more urgent when we consider its fundamental importance for the planning of research.

The work of the Association of Official Agricultural Chemists in developing and improving the methods of analyses has been of the very greatest value. The methods which we now follow are largely of the rule-of-thumb order, but the rule of thumb is better than no rule at all. That we are all working by the same methods, and those the best that in the present condition of our knowledge we can devise by united effort, is far better than that we should work by methods differing from one another, and each no better, and in general not so good as the common method which we follow. And one of the most valuable results of the efforts of the association has been to bring into clear light, to emphasize, and in a measure explain, the need of improvement of methods.

It is one thing to be drifting helplessly in an unknown sea, and quite another to know exactly where we are and in what direction our port lies. We are finding out a little as to our situation, our bearings and distances. We want a map which will show us just what exploration has discovered; then by united effort we can gradually and truly learn about the currents, the coasts, the reefs and where the harbors are.

HOW SHALL THE WORK BE DONE?

The information as to what has been learned can be best collated by the coöperation of specialists. This could be accomplished through the Department of Agriculture. We have a considerable number of men in the United States who have devoted large amounts of time to the study of particular branches of the general subject. Some of them are connected with the Experiment Stations and Department of Agriculture; others are professors and instructors in colleges. For branches of the subject in which there are no specialists on this side of the Atlantic it would be well if the services of leading European specialists could be secured.

For the prosecution of the necessary investigations coöperation of a large number of specialists will of course be requisite. We may confidently expect that Experiment Stations will be able to devote more and more labor to this higher research. Its scientific value is such that chemists in our colleges and universities ought to be led to join in it. Is it too much to suggest that international coöperation might be secured? One essential is the means for paying the expenses of the work. For this a small amount of money would do a great deal. There are many investigators in the country, both those who have already acquired reputation and influence and those who are ambitious to secure them, who would gladly give their time and thought to investigations in their several specialties, the combined results of which would bring the needed information, if they could only have the means for defraying the expense. A hundred dollars here, two hundred there, and five hundred in another place, would bring the results for which thousands would be necessary if the work was to be done by men especially employed and paid.

In what the Smithsonian has done in times past in promoting research by small amounts of money we have an illustration of what might be accomplished here. The result would be useful in several ways; it would encourage research, develop talent, and improve the intellectual tone of the institutions where such work was being done; its influence upon the development of science in the country would be excellent, and the practical values of the outcome would many times exceed the cost.

Might not the association make good use of the influence which it has gained by endeavoring to secure from the institutions with which it is connected and from the Government, through the Department of Agriculture, the means which would contribute to so desirable a result?

Mr. Myers moved that the report be accepted as a report of progress, that the committee be authorized to take such steps in coöperation with the reporters on foods and feeding stuffs as would, in their judgment tend to promote the objects desired, and that the committee be continued. Carried.

Mr. Huston read the following paper:

NOTES ON THE OCCURRENCE AND QUANTITATIVE ESTIMATION OF THE PENTAGLUCOSES IN FEEDING STUFFS.

By W. E. Stone.

It is desired to call the attent on of those chemists interested in the analysis and valuation of foods to the results of some study of the pentaglucoses as food constituents. By the term pentaglucoses we understand a group of sugar-like bodies with the general formula $C_5 H_{10} O_5$, belonging therefore to a distinctly different series of derivatives from the true glucoses or the true carbohydrates. The bodies do not occur free in nature as do the true glucoses, but my observations go to show that the peculiar class of gum-like bodies from which they are derived are of common and abundant occurrence in most vegetable products. These pentaglucoses are two in

number so far as is yet known, viz, *arabinose* and *xylose*. Arabinose may be prepared by the action of dilute acids upon certain gums, such as gum arabic, gum tragacanth, cherry gum, peach gum, etc. More than this, if we extract different forms of vegetable tissue with weak alkalies we have in solution gum-like substances which are abundantly precipitated by alcohol, and which by hydration with dilute acids also give, in some cases, *arabinose* and in others *xylose*. In this way these pentaglucoses have been actually isolated from sawdust, straw, bran, brewers' grain, the pulp of sugar beets, etc. Concerning the nature of these gums which give rise to the pentaglucoses we know little. The name *gum* is perhaps ill fitting, but is retained here for convenience. Whether the gums, such as gum arabic and cherry gum, produced under abnormal conditions are similar to those materials extracted from plant tissues by alkalies is questionable, but they at least seem to bear the same relation to the pentaglucoses. This relation we may compare in a very general way to that between starch and glucose, *i. e.*, the hydrating effect of acids converts the one into the other.

My earlier observations have established that the pentaglucoses differ from the true glucoses by one characteristic reaction. They yield, when slowly distilled with strong acids, large quantities of furfurol. No member of the true glucoses or any of the bodies from which they are derived will respond to this reaction. Arabinose and xylose yield, on the other hand, about 50 per cent of their weight in furfurol. Not only this, but all of those substances from which the pentaglucoses have been prepared also yield corresponding quantities of furfurol. Hence this becomes a reaction for the recognition in crude vegetable products of the pentaglucoses or the bodies from which they are derived. The application of this test consists in distilling a small quantity (about 5 grams) of air-dried material with sulphuric acid of 1.254 specific gravity during several hours at 125° to 135°. The furfurol formed is collected in the watery distillate, and in order to maintain the acid at a constant concentration water is allowed to drop slowly into the distilling flask at a rate corresponding to the distillation. The furfurol is estimated in the distillate by concentrating the same by fractional distillation and precipitating with dilute ammonia as furfuramid, in which form it is dried and weighed. The furfuramid thus obtained stands in the relation to the pentaglucose of 1 to 1.679, that is, the percentages given below need to be increased by nearly four-fifths in order to give us their equivalent in actual pentaglucoses.

Forty common materials, selected with the view of obtaining as great variety as possible, have been examined for the occurrence of the pentaglucoses. In the following thirty appreciable quantities were recognized.

Material.	Furfuramid in air-dry substance.	Material.	Furfuramid in air-dry substance.
	Per cent.		*Per cent.*
Hungarian grass	3.34	Corn cobs	8.16
Timothy hay	1.18	Gum arabic	5.46
Clover hay	1.55	Gum tragacanth	8.08
Clover ensilage	0.40	Cherry gum	8.14
Corn stover	2.89	Peach gum	4.84
Maize ensilage	0.91	Manure from cattle fed on maize ensilage.	2.88
Malt sprouts	1.82		
Brewers' grain	7.20	Manure fron cattle fed on corn stover	3.94
Wheat straw	4.16	Seeds of white lupine	0.95
Oat straw	2.29	Seeds of yellow lupine	1.69
Cotton-seed hulls	3.66	Coats of orange seeds	1.85
Corn bran	1.80	Orange peel	0.69
Corn cob meal	0.59	Watermelon seeds	2.70
Linseed meal	1.27	Pulp of strawberries	1.95
Oatmeal	0.40	Beet pulp	3.59

Eight substances examined did not yield appreciable quantities of furfuramid, but still gave fine qualitative reactions for furfurol.

They were, cotton-seed cake, corn meal, sweet potatoes, kernels of orange seeds, raw coffee, buckwheat, dried strawberries, and beans.

This list might be greatly extended, yet it suffices to prove the common occurrence of the pentaglucoses, respectively the bodies from which they are derived, and that, too, in considerable quantities, ranging from 1 to 12 or more per cent.

As regards the behavior of the pentaglucoses to Fehling's solution, their reducing action has been known as long as the bodies themselves, but their *quantitative* reaction had not been worked out. For *arabinose* I have determined the constants for solution of 1 per cent or less by the gravimetric method, and find that it is more strongly reducing than any sugar yet studied. Without reviewing this work in detail, it may suffice here to compare the amount of arabinose and the true sugars necessary to precipitate the copper in 1 cubic centimeter of Fehling's solution, as follows:

	Mgr.
Arabinose	4.532
Dextrose	4.753
Lævulose	5.144
Invert sugar	4.941
Galactose	5.110
Milk sugar	6.757
Maltose	7.780

Of this list, therefore, arabinose is the most strongly reducing. The other pentaglucose, *xylose*, has not yet been studied in this relation, but the work will soon be undertaken, and there is no reason to doubt that it also will differ from the true carbohydrates in this respect.

We see, therefore, that here is a group of common food constituents which have heretofore been classified with the carbohydrates or non-nitrogenous extract matter, but which have distinct characteristics and, it is safe to assume, special food values of their own. Let us consider the importance of their recognition as food constituents.

It is a notorious fallacy of our food analyses that under the term "non-nitrogenous extract matters" we collect a great number of different bodies of very unlike nature, although in our food valuations and digestion experiments we assume a homogeneous composition and behavior for them. This class of bodies often reaches a very high percentage of the food, so that the error is exaggerated. It appears, however, from the foregoing results that it is possible to differentiate from the others a specific class of compounds which, while they resemble carbohydrates, have undoubtedly a different digestibility and food value. For instance, in the list of materials examined it appears that these pentaglucoses or their gums induced the action of destructive processes of the silo in both maize and clover.

Again, they were found in large quantities in the manure of animals fed on at least two different rations. Yet the ordinary food analysis would leave us no ground for distinguishing between these and the true carbohydrates, like starch, glucose, etc., which we know easily yield to fermentation and digestive action. The most cursory examination shows us at once that here is a source of error in our methods of measuring food values, digestive action, etc.

Again, in their relation to analytical methods we note that here are compounds which we may easily compare with the glucoses, but which have an entirely different origin. Suppose a determination of starch to be made in any material by means of inversion and titration with Fehling's solution. Accompanying the starch we may have an indefinite quantity of the pentaglucose gums. The same action which converts the starch into glucose also changes these gums into pentaglucoses, and the results obtained with the Fehling's solution are ascribed to starch when they may be due largely to something quite different. To suppose an extreme case, an examination of brewers' grain, which, if thoroughly fermented, contains no starch or glucose, might still give us results which could, according to present views, be only interpreted as indicating 10 or 12 per cent of starch, while actually it came from the pentaglucose gums, which are not destroyed by fermentation.

Having pointed out thus briefly (without reference to the details of work on which

the conclusions are based, and which will be published presently) the importance of this class of food constituents, it is next desirable that some methods for their speedy and convenient recognition be developed. Such a method must rest upon their characteristic reaction of yielding furfurol under certain conditions, since in most other respects they resemble closely the true carbohydrates. Such a method must also enable us to recognize these bodies in the presence of other compounds and without previous manipulation of the material.

The method has already been developed on these lines to that point where its eventual success seems assured, although it is at present far from perfect. It consists of two phases:

(1) Conversion of the pentaglucoses or their gums into furfurol.

(2) The determination of the furfurol.

The first phase has thus far been accomplished by distilling the material to be examined with strong sulphuric acid of specific gravity 1.254 at a temperature of 125° to 135°, the distilling flasks being placed in a paraffin bath and connected with a condenser for collecting the furfurol and with a water reservoir for supplying the loss by distillation. The process lasts eight to twelve hours.

To determine the furfurol two methods have been followed: the one already mentioned, and by which the results given were obtained; the other, since worked out, consisting in titrating the furfurol containing distillate with a standard solution of phenyl-hydrazin, detecting an excess of the latter by means of its powerful reducing effect upon Fehling's solution in the cold.

This method of determining the furfurol is rapid and accurate. The most difficult part of the entire process is the distillation, in which the conditions are hard to control, and yet successive determinations have been repeatedly obtained not varying more than 0.2 to 0.3 per cent from one another. The development of this method is still in hand, with good prospects of successful solution. Meanwhile this communication is submitted for the purpose of calling attention to the existence of an important and abundant class of bodies not heretofore recognized in our consideration of the composition and analysis of foods.

Mr. Huston said that Mr. Stone was very modest in regard to the second of the analytical methods which he had worked out; the process was an exceedingly short one for titrating the furfurol.

Mr. Cooke said that lest the members of the association should go home with the idea that the work they had done upon the samples during the past year was not so good as that done the year before, he had figured out a few of the differences. He presented the following table:

Material analyzed.		Per cent of members agreeing within 0.50 per cent on the fat determinations.	Per cent of members agreeing within 1 per cent on fiber.
Hay	1889	20	61
	1890	53	65
Bran middlings	1889	70	
	1890	90	
Cotton-seed meal	1889	70	
Linseed meal	1890	88	

Mr. Wiley presented the following report:

NOTES ON METHODS OF SUGAR ANALYSIS.*

By H. W. Wiley.

The subject of the analysis of sugar would be appropriately introduced by a general statement concerning the difficulties which have been encountered heretofore in securing uniformity in this class of work. Briefly, I may say that these discrepancies in analytical results have been due, especially, to three causes, viz:

First, inexperience on the part of analysts; second, imperfections and variations in the instruments employed; and third, variations in the standards which have been used.

In regard to the first question it can only be said that the difficulties encountered from this source can only be removed by a more careful consideration of saccharimetric methods and a greater degree of careful practice on the part of analysts. It is reasonable to expect that the same degree of improvement which has characterized other lines of research in which the Association of Official Agricultural Chemists has been engaged will attend any efforts in this direction.

In regard to the second difficulty, viz, the use of different instruments and instruments which have been differently graduated, a less degree of progress must be expected. It is not always easy to determine in any given way what method of graduation has been followed in the standardization of any optical saccharimeter which may be in the analyst's hands. The truly scientific method of graduating an optical saccharimeter would be the use of the absolute cubic centimeter, *i. e.*, the volume occupied by 1 gram of water weighed in vacuo, at 4° temperature, and the use of absolutely pure sugar weighed in vacuo for fixing the 100° point on the scale.

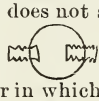
In point of fact, however, different manufacturers use different methods for the graduation of their instruments. Instead of the true cubic centimeter, as described, it has been very common to use what is called the Mohr cubic centimeter, viz, taking as 100 cubic centimeters the volume occupied by 100 grams of water at a temperature of 17.5°. In the Schmidt and Haensch instruments it is stated by them that the Ventzke scale which is used by them is obtained by the solution of 26.048 grams of pure sugar in 100 cubic centimeters of water at 17.5°, and that the specific gravity of the solution is 1.10 and that its angular rotation in a 200 millimeter tube is equivalent to $(a)D = 34.55$. This is the method of standardization which they give in their printed instructions to guide analysts in the use of their instruments. In a recent letter, however, received from them they inform me that the true value of the Ventzke degree is expressed by the equation $(a)D = 34.68$, which is quite a different number from that given in their printed instructions, viz, 34.55.

For the daily control of an optical saccharimeter there is, perhaps, nothing superior to a first class quartz plate, the value of which has been tested against pure sugar. The danger, however, of using a quartz plate at its marked value is so great that I need not caution the members of the association against it. The quartz plate also has different values, according to the position in which it is placed in the instrument, so that its value should be fixed once for all by comparison against a pure sugar solution. A control tube may also be used which can be made of variable length by a ratchet and scale moving over a carefully graduated vernier, using pure sugar solution for charging the tube. An optical saccharimeter should thus be carefully tested at each 5 degrees from zero to 100°, and any inaccuracy in the scale noted and allowed for in practical work.

In regard to the kind of instrument which is to be employed this must be left to

*An extensive bibliography of articles relating to sugar analysis has been prepared. On account of its great length it is here omitted, and will be published subsequently as a separate bulletin.

the preference of the analyst. There are, however, three classes of instruments which have met with general approbation, and it is earnestly suggested that the analysts connected with this association confine themselves, at present, to one of these classes. These are the Laurent instrument, the Scheibler color instrument, and the Schmidt and Haensch shadow instrument. For ordinary work the Schmidt and Haensch shadow instrument with a single scale is quite efficient; for accurate work their instrument with double compensation is to be recommended. The method of adjusting the double compensating instrument is as follows:*

"Before instrument No. 1427 can be used it is necessary to control the zero-point. After the red scale has been placed on zero the wedge corresponding to the black scale is moved until the field exhibits the same tint throughout. The black nonius should then point exactly to zero. If this is not the case the wedge is moved by means of the micrometer-screw on the left until absolute zero is obtained. The correctness of this zero is determined by repeated trials. If now, after both scales are placed at zero, one side of the field appears colored we must proceed as follows: The wedges are removed and the color of the field observed. The large wedges are removed by screwing them out as far as they will go and then simply pulling them out; then the two screws *a* and *b* are removed and the small wedges taken out. If now the field does not show an even tint the analyzer is moved by the two screws placed at the  side, loosening one and tightening the other correspondingly until the desired result is reached. The small wedges are now put back in the order in which they are marked, the large wedges placed in position, and the zero point corrected as before. The zero point of the instrument is now accurate, and if the divisions of the scale are correct the quartz plate should give the correct reading. If, however, an incorrect reading is obtained, the plate should be taken out and controlled by means of the red scale. If this gives the correct reading the black scale is wrong, otherwise both scales are inaccurate.

"The scales of the instruments are prepared by means of a number of normal quartz plates, whose values have been determined by several German, Austrian, and Belgian scientists and chemists. A control determination of these values is made every two years. An official examination of the quartz plates has never been made. Various chemists at times attest the accuracy of our instruments. For the last fifteen years our instruments have been sold under our own guaranty and during that time many chemists have tested them and never found an error. We may therefore consider our guaranty as sufficient.

"Ventzke's scale is based on 26.048 grams chemically pure sucrose of the specific gravity 1.10 in 100 cubic centimeters of water at 17.5° C.

"It is different with the French scale. This is based on the equivalent rotation of chemically pure sucrose and a 1 millimeter quartz plate.

"On account of these different methods of division the normal rotation for D light gave for 1 degree Ventzke = 0.3455 circular degrees and 1 degree Ventzke on the French scale = 0.3457 circular degrees.

"(See Landolt, Das optische Drehungsvermögen organischer Substanzen, page 162, and Chemisch-physische Tabellen von Landolt und Börnstein, page 230.)

"We are now confronted by the question: Are the values 0.3455 and 0.3457 per circular degree correct?

"Some years ago we personally made determinations of the Ventzke degrees with D light and at that time found 1° Ventzke, white light = 0.3463, resp. 0.3464 circular degrees D light. Your communication caused us to repeat these experiments with the improved saccharimeters at hand, which gave the following result:

1° Ventzke white light = 0.3467 circular degrees D light.

"We do not know whether the values given by Landolt and in the tables have been lately corrected; our carefully and accurately made experiments have nevertheless given different results.

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* Communication from F. Schmidt and Haensch.

"Some time ago we asked the Physical-Technical Institute to make extended experiments on the constancy of the rotatory power of various kinds of quartz, to establish a normal, and thus lead to the adoption of an international scale for all saccharimeters. Our request has been favorably considered, and we may soon expect satisfactory results which will throw more light on this subject.

"We will not fail to communicate with you as soon as these investigations are completed and published."

The graduation of the Laurent instrument is fixed in such a way as will give for 16.19 grams of pure sugar in 100 true cubic centimeters a value of 100° on the scale, corresponding to an angular rotation of 21.67 for $(a)D$.

The Scheibler color instrument is graduated also by the Ventzke scale, the same as is used by Schmidt and Haensch in their shadow instruments, giving, in sugar degrees, for 26.048 grams of pure sugar dissolved in 100 cubic centimeters, one hundred divisions equivalent to an angular rotation of 34.55 or 34.68, as given above.

The variations which may be caused by weighing in air instead of weighing in vacuo must also be taken into account. A flask standardized by weighing the calculated amount of water into it in air will be to a true 100 cubic centimeter flask, graduated in vacuo, as 100.155 cubic centimeters is to 100 cubic centimeters. The error of weighing the sugar in air may also be deduced from the following proportion, viz, 26.048 grams of sugar weighed out in air are equivalent to 26.064 grams weighed in vacuo. In making up a sugar solution, weighing 26.048 grams in the air and standardizing the flask in the air, each cubic centimeter of the solution will contain .260236 gram of sugar. A Mohr flask graduated to hold 100 grams of water at 17.5° has the following relation to a true 100 cubic centimeter flask, viz, 100.12 : 100 cubic centimeters. Instead of a true 100 cubic centimeter flask at this temperature holding 100 grams, as a Mohr flask does, it holds exactly 99.8747 grams of water.

These points must all be taken into consideration in the actual standardization of instruments. I think it is necessary that we should obtain a certificate of each instrument used from its maker stating the method of its graduation, and then use with that instrument the same flask and same weights which were employed in obtaining this graduation. If the instrument is used with a Mohr flask containing 100 grams of water weighed in air at a temperature of 17.5°, then we should use Mohr flasks for our analyses. If, on the other hand, the instrument is graduated by a true 100 cubic centimeter flask containing 100 grams of water at a temperature of 4°, then all our flasks should be graduated in this way whether they be weighed in air or in vacuo. In the same way, if the standard weights of sugar used in graduating the instrument are weighed in air, we should make our weighings in air; if, however, the standard weights of sugar are corrected for weight in vacuo, then we should correct also for weight in vacuo.

ABSTRACTS RELATING TO SUGARS AND ANALYTICAL METHODS.

INVERT SUGAR.

Jungfleisch and Grimbert* have shown that the rotatory power of pure levulose when observed directly differs much from that which is derived from observation in corresponding circumstances of an invert sugar considered as a mixture of equal weights of glucose (dextrose) and levulose.

Clerget's numbers obtained in 1849† have been confirmed by Tuchschmid.‡ Tuchschmid's formula was $\alpha D = -(27°.9 - 0°.32t)$, which is applicable to a liquor containing 17.21 grams of inverted sugar in 100 cubic centimeters. At different temperatures the rotatory power of pure levulose compared with the rotatory power of levulose calculated from invert sugar is as follows:

	Temperature.				
	0°.	5°.	10°.	14°.	20°.
αD pure levulose	101.22	98.42	95.62	93.38	90.02
αD levulose, calculated from invert sugar	108.54	105.34	102.14	99.58	95.74

These differences are probably due to certain unexpected peculiarities produced by the action of acids upon the levulose.

(1) It is shown that the rotatory power of crystallized levulose is not affected by the introduction of equal weights of dextrose; this last sugar, therefore, can not produce the differences noted.

(2) When pure levulose is subjected to the treatment by which invert sugar is made from cane sugar, it is found that its rotatory power is strongly affected. A solution of pure levulose which at 12° gave $\alpha D = -94.66°$, gave $\alpha D = -96.78°$ when it had been previously treated with 5 per cent strong hydrochloric acid and heated to 68° for half an hour. When sulphuric acid was employed the rotatory power was still more highly increased, reaching $\alpha D = -99.77°$. These results were not notably affected when the acids were carefully neutralized before the observation was made. Oxalic acid acts like the mineral acids in this particular. Acetic and formic acids are without effect. In 1846 Dubrunfaut § showed that the rotatory power of inverted sugar varied with the nature and proportion of the acid employed. A solution of cane sugar, inverted according to the method of Clerget, showed the rotatory power of the levulose $\alpha D = -101.3°$; while the same solution inverted by another method, that is the addition of 5 per per cent of hydrochloric acid and heated to 68° for thirty minutes, showed $\alpha D = -96.52°$. It is also demonstrated that acetic and formic acids employed with 5 per cent strength and at 100°, invert cane sugar completely in thirty minutes and give a liquor whose rotatory power remains constant even after prolonged heating, and in the invert sugar thus obtained the levulose possesses the rotatory power of pure levulose. In the conditions where pure levulose gave $\alpha D = -94.66°$ we found after inversion with acetic acid for thirty minutes at 100° $\alpha D = -94.75°$; and after heating for one hour $\alpha D = -94.48°$, after heating with 10 per cent acetic acid for one hour $\alpha D = -94°$; after heating with 5 per cent formic acid at 100° for thirty minutes $\alpha D = -94.80°$. Moreover, it was seen that when hydrochloric acid was added to the solution inverted as above, the levulose underwent modifications similar to those which pure levulose suffers in the

* Comptes rendus, Vol. 107, p. 390.

† Anuales de Chimie et de Physique, 3d series, Vol. 26, p. 175.

‡ Journal für prakt. Chemie, Vol. 2, 1870, p. 135.

§ Comptes rendus, Vol. 23, p. 38.

same circumstances. The conclusions reached by these experiments were as follows:

(1) Strong acids modify the rotatory power of levulose by increasing it more or less according to circumstances.

(2) The levulose of sugar inverted by the processes in ordinary use is not strictly identical with pure crystallized levulose.

Maumené* criticises the experiments of Jungfleisch and Grimbert, the abstract of which precedes, in a long article which in many places seems permeated with strong personal feeling. As a resumé of his criticism he states: First, inverted sugar, even when inverted by pure water, is never a mixture of equal weights of glucose and levulose or even of chylariose. Second, glucose is a mixture of several hexeloses; one of these, left-handed hexelose, approaches very near in its composition to what is called levulose derived from inuline. It is very difficult to isolate it even at a freezing temperature, and it is unstable in a higher temperature. Another, optically neuter, which has been called inactose, is obtained by a complete transformation of normal sugar by means of nitrate of silver. The third is a non-fermentable hexelose. It occurs in the inversion of normal sugar by pure water or even by water which has been treated with a few ten-thousandths of acid. It is separated from the others by fermentation. The character of invert sugar is influenced, first, by the relative quantities of sugar, water, and acid; second, by the degree of heat; third, by the time of the reaction; fourth, temperature during the subsequent treatment with lime, saturation of the products by carbonic acid and the duration of the evaporation in a vacuum.

Inversion is produced by a series of molecular movements modified by these numerous influences, and the greatest precautions are necessary to obtain the same result even in like conditions.

Glucose preserves a certain quantity of a mixture of hexeloses properly named chylariose, since it is extracted from the inverted sugar by capillary attraction, porous brick or porcelain, or blotting paper.

Jungfleisch and Grimbert have confirmed the alteration of left-handed hexelose or levulose, not upon this hexelose properly so called, but upon the inverted sugar by a comparison with a product of inuline, a product which can not be assimilated to inverted sugar without many errors.

The specific rotatory power of cane sugar is generally acknowledged to be independent of temperature. If, however, a solution of sucrose be made up to the standard volume of 100 cubic centimeters at a certain temperature and then polarized at different temperatures, it will show either an apparent increase or decrease in rotatory power as the temperature is lowered or raised. This is simply due to the fact of the contraction of the solvent, thus admitting a larger number of sugar molecules in a given length of the column at a low temperature than at a high temperature.

Wartze† has determined this change in polarization in a large number of instances, and finds that the polarization expressed in degrees of cane sugar in a normal solution (26.048 grams in 100 cubic centimeters) changes about 0.1 of a degree for each difference of 2° in temperature. A solution polarized at 14° gave a reading of 95.6. The same solution polarized at 34° gave a polarization of 94.7; for a difference of 20°, therefore, the difference was 0.9 of 1 degree. In another experiment a difference of 24° showed a difference of 0.1 of a degree in polarization. On changing the temperature back to the original the original polarization was obtained. A solution that, polarized at 17°, gave 95.1° polarization, when cooled to 10° showed 95.5° polarization; when reheated to 17° it showed again 95.1°.

(From these numbers the importance of making the polarization at the temperature at which the solution is made up is at once seen. For this reason the solutions should all be made up at a given temperature in a place near that where the polarizations are

*Abstract from Journal des Fabricants de Sucre, March 27, 1889.

†Deutsche Zuckerindustri, April 20, 1889. La Sucrerie Belge, June, 1889, p. 441.

made, and the temperature should not be allowed to change from the time the solutions are made up until the polarizations are complete.

As has already been said, most sugar flasks are graduated either at 15° or 17.5°. The mean temperature of laboratories in the United States is much higher than this, and it would probably be well to have all our flasks graduated at about 22°. Since, however, the volume of a flask will change very little within the limits given, viz, 15° to 22°, it is more important that the polarizations be made at the same temperature at which the solution is made up than that all the flasks should be graduated at a given temperature.—H. W. W.)

ABSTRACT OF A. WOHL'S PAPER ON CHARACTER OF THE CARBOHYDRATES.*

Kirchoff, in 1811, noticed the change of starch into dextrose by heating with acids, and Biot the changes in rotatory power produced in cane sugar by the same reagent. The tendency of all polysaccharides to be reduced to monoses has given rise to a rich literature. Further treatment of the monoses results in the formation of humus substances and of organic acids.

The important observation of Grimaux and Lefevre of the reformation of dextrinoids by heating pure glucose with HCl is also made the basis of some interesting deductions.

The time element in inversion has been studied by Wilhelmy and others. The invertive power of very small quantities of mineral acids in concentrated sugar solutions is pointed out, especially with a mere trace of HCl, which, when melted with sucrose, secures a complete inversion thereof, and that, too, without notable discoloration. Illustrations are given of the action of HCl on concentrated sugar solutions.

13.024 grams of sucrose were heated for thirty minutes in a stoppered flask at 100°, and then showed a polarization of 12°. With longer heating the left-handed polarization diminished, and also the quantity of copper precipitated. It is concluded from the diminution of the left-handed polarizing power of the invert sugar, caused by concentration of the solution and of the acid and by high temperature and duration of the invertive process, that the invert sugar formed is not pure levulose and dextrose but also contains a different sugar. If this diminution be due to a molecular condensation of the invert sugar formed, then it would take place also when pure invert sugar is heated with an acid. This experiment was tried with invert sugar and hydrochloric acid. Pure dextrose and levulose were used for these experiments. 3.425 grams of each were taken and made up to 50 cubic centimeters at 20°, polarizing 15.8°. 0.1714 gram of the mixed sugars gave 0.313 gram copper. On heating this, as before, with dilute HCl, both polarization and reduction were diminished. Heating with water alone gave no change, so that the condensation of the molecules of invert sugar is due to heating with acids.

It was necessary, in order to elucidate the problem further, to note the action of HCl on concentrated glucose and levulose solutions. These results showed that the dextrose was but little affected by the treatment, and hence that the changes noted had been due to polymerization of the levulose.

An examination of the products formed by the action of a small quantity of acid on concentrated levulose solutions shows that dextrin-like (levulin-like) bodies are formed (levulosin). An 80 per cent solution of dextrose was heated at 105° with increasing quantities of acid. This treatment increased the polarization of the substance, and diminished its reducing power, indicating a polymerization and formation of dextrinoids. Whence it follows that the hydrolytic splitting up of the di- and poly-saccharides is not a simple process, but, together with the inverting action of the acid shown in the splitting up of the higher molecular weights, there is a synchronous reformation of the polymers. These phenomena give support to the opinion

* Berichte, July 14, 1890, pp. 2084 *et seq.*

of Tollens, that the monoses are not pentaoxyaldehydes or pentaoxyketones but pentaoxyoxides, that is, aldehyd or keto-γ-lactones, in which the structural formulæ for dextrose and levulose are as follows:

Dextrose.

$$CH_2(OH)CH(OH).\ CH.\ CH(OH).\ CH(OH)CH(OH).$$
$$\text{——————O——————}$$

Levulose.

$$CH_2(OH)CH\ CH(OH).\ CH(OH)C(OH)C(OH)CH_2OH.$$
$$\text{——————O——————}$$

It is further shown that the usual methods of inversion use, without exception, excessive quantities of acid, and that the maximum levogyrous result and maximum reducing power are to be obtained only with very dilute acids or at low temperatures.

In order to convert pure sugar into colorless invert sugar it is only necessary to heat the solution at 95° for a half hour with 0.01 per cent HCl.

The above principles of inversion were also applied to starch, inulin, etc., on the supposition that the difficulty of securing a complete inversion of starch lay in the reformation of dextrin by the strong acid employed rather than in the natural refractory nature of the material, and experiments are given supporting this hypothesis.

Pure levulose.—Directions are given for the preparation of pure levulose as follows:

In an Erlenmeyer flask of 50 cubic centimeters, capacity put 50 cubic centimeters water and 5 cubic centimeters of HCl of a specific gravity sufficient to give 0.01 to 0.02 per cent HCl to weight of inulin. (For 200 grams inulin of 0.25 per cent ash content, 5 cubic centimeters normal HCl; for higher ash content, more). The 200 grams inulin, in fine powder, are then added, well shaken, and heated in boiling water (not in bath). After thirty minutes from the time mass is evenly heated the maximum of inversion is reached, the flask is removed from the boiling water. The sirup carrying some granules of inverted inulin is poured into one liter of warm absolute alcohol; a little blood carbon added and allowed to stand twenty-four hours and filtered. A few crystals of fruit sugar added to the filtrate causes a copious crystallization of pure levulose. A better yield is secured by evaporating the alcoholic filtrate to a thick sirup, and putting over H_2SO_4 in desiccator. A crop of crystals is thus obtained which resemble dextrose got in similar conditions. The crystal masses thus obtained are dissolved in three to four parts absolute alcohol, allowed to stand twelve hours, and the clear solution poured off. A few crystals of fruit sugar and rubbing with a glass rod cause the crystallization of the levulose to appear at once.

SOME FACTS RELATIVE TO THE ANALYSIS OF SUGARS.

By JUNGFLEISCH AND GRIMBERT.*

Some facts which have been developed in the experience of the authors lead them to doubt the principle of the method of Clerget. The process of Clerget may be expressed as follows:

Let A be the deviation produced by 1 decimeter of the liquor in which it is desired to find the weights x and y of the sucrose and of the inverted sugar. Let A′ represent the deviation of the same liquid inverted by strong acid without changing its concentration; then $(a)_D = 67.31$ and $(a)_D = -24.31$, this being the expression for the rotatory power of the sucrose and inverted sugar; then the two equations which will give the value of x and y are as follows:

$$\frac{67.31}{100}x - \frac{24.31}{100}y = A;\ \text{and}\ \frac{24.31}{100}(x+y) = A'.$$

* Comptes rendus, vol. 109, p. 867.

The results obtained in this way are generally inexact. Contrary to what is supposed in the first equation, inverted sugar exists in natural sugar products which have not been subjected to the action of strong acids and its rotatory power, which at first is about $(\alpha)_D = -21.16$, increases greatly during inversion.

Therefore the calculation indicates a plus error for the second an error proportionately to $\frac{y}{x}$, this increasing with the weight of inverted sugar preëxisting; moreover, the calculation exaggerates the error committed.

It is known that if such a sugar be treated with strong and dilute acids, the product is always more strongly left-handed in the first than in the second case. When analysis is made on crystallized sugar of commerce, which is always poor in inverted sugar, the difference is very little and may be neglected, but such is not the case with sugars rich in inverted sugar. When the substances analyzed contain glucose and levulose in unequal quantities, the other compounds are sometimes determined by the aid of an analagous calculation by estimating a third equation from the reduction of alkaline copper solution, but the same objection still applies. Acetic acid acts upon saccharose without modifying the levulose, but with certain salts certain facts have been established which tend to prevent its general use. These facts may be summarized as follows:

(*a*) Alkaline acetates, although they do not prevent the inversion of sucrose by strong acids employed in excess, interfere with the inversion by acetic acid even when employed in very great excess. In presence of 1 molecule of acetate of soda 1 molecule of sucrose is not completely convêrted even at 100° during a half hour by a weight of acetic acid equal to 80 molecules.

(*b*) Alkaline citrates, formiates, lactates and tartrates, the acetate of zinc and lead act in a similar manner. The acetate of lime is much less active.

(*c*) The salts of strong monobasic acids do not prevent inversion by acetic acid. The neutral salts of strong bibasic acetates diminish the inverting power when the base is monovalent, but not when the base is bivalent. The acid salts of strong polybasic acids do not retard the inversion by acetic acid, but sometimes even effect it themselves.

Details of the work will be given in a future memoir.

ESTIMATION OF GLUCOSE WITH ONE-TENTH NORMAL COPPER SOLUTION, ACCORDING TO SOLDAINI'S METHOD.*

To avoid the decomposition of stronger solutions, such as the normal solution, Soldaini proposes the use of a one-tenth normal solution made as follows: 3.464 grams crystallized copper sulphate ($CuSO_4 + 5H_2O$) and 20.7 grams of $KHCO_3$ dissolved in 1,000 cubic centimeters of water. For the estimation of glucose with the one-tenth normal solution, 100 cubic centimeters of this solution are heated to boiling and the glucose solution added gradually until complete reduction takes place. The 100 cubic centimeters of the one-tenth normal solution correspond to 0.05 gram glucose.

QUICK ESTIMATION OF SUGAR BY ONE-TENTH COPPER SOLUTION.

By J. E. Politis.†

The one-tenth copper solution is made as follows: 24.95 grams crystallized copper sulphate, 140 grams of the tartrate of sodium and potassium, 25 grams caustic soda. The above substances are dissolved in distilled water, mixed together, and the mixture made up to 100 cubic centimeters. There is also required a one-tenth normal hyposulphite solution made as follows: 24.8 grams pure crystallized hyposulphite of soda dissolved in distilled water and made up to 1 liter. There is also required a

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*Chemisches Central-Blatt, No. 9, 1889, volume 2, p. 389. †*Ibid.*, p. 390.

one-tenth normal iodine solution made by dissolving 12.7 grams of iodine in alcohol and making the volume up to 1 liter. The titration is performed as follows: 50 cubic centimeters of the copper solution is heated to the boiling point. There are then added 10 centimeters of the sugar solution, which is allowed to boil, made up with water to 100 cubic centimeters, and 50 cubic centimeters filtered off. The filtrate is made slightly acid, and iodide of potash added in slight excess, together with some starch solution, and the iodine which is set free is titrated with the solution of hyposulphite which corresponds to the copper which has not been reduced. The one-tenth normal solution of iodine serves for determining the strength of the hyposulphite of soda solution. Full details of this method will be found on page 145.

ESTIMATION OF SUGAR BY FEHLING'S SOLUTION.

By H. Causse.*

To 10 cubic centimeters of ordinary Fehling's solution are added 4 cubic centimeters of a 5 per cent solution of potassium ferrocyanide and 20 cubic centimeters of water. On the precipitation of the cuprous oxide by reducing sugar, the potassium ferrocyanide dissolves it as soon as it is formed, preventing the occurrence of a yellow color and keeping the reagent perfectly clear. The disappearance of the blue copper color is taken as the end of the reaction. The author of this method says that the potassium ferrocyanide is without action either on hot or cold Fehling's solution. On cooling the liquid turns brown and deposits colorless crystals.

Note.—The above method was tried in my laboratory with the following results: A solution containing reducing sugar gave, according to the usual method, 15.7 per cent; with the addition of the amount of ferrocyanide mentioned above, it showed 13.1 per cent. When 13.1 per cent of the sugar solution were run into the Fehling's solution without ferrocyanide, the blue color was still distinctly marked, even in the presence of the yellow cuprous oxide. From the above it is seen that a part of the copper seems to be consumed by the ferrocyanide, probably with the production of ferricyanide. The method, therefore, is not applicable.—(H. W. W.)

ESTIMATION OF RAFFINOSE.†

Let x = sugar in 100 cubic centimeters.
y = raffinose in 100 cubic centimeters.
P = rotation before inversion.
P′ = rotation after inversion at temperature t.

$$102x + 158.4y = 16.20\text{P}.$$
$$-(44 - 0.5\,t)\,x + (75 + 0.5\,t)\,y = 16.26\ \text{P}'.$$

(whence $y = 16.26 \times \dfrac{(44 - 0.5\,t)\,\text{P} - 102\,\text{P}'}{158\,(44 - 0.5\,t) + 102\,(75 + 0.5\,t)}$

The operation is carried on in the following manner:

One hundred grams of sugar are shaken for some time in a flask of 250 cubic centimeters capacity, with a narrow neck, with 150 cubic centimeters of methyl alcohol to which a few drops of alum have been added. One hundred cubic centimeters of the solution are taken and distilled in a flask until about 40 cubic centimeters of the alcohol has distilled over. Twenty cubic centimeters of water are then added to the flask and afterwards some subacetate of lead, until no further precipitation is produced. A small quantity of moist alumina is then added, the volume made up to 100, filtered and polarized. Fifty cubic centimeters of the filtered liquid are evaporated to drive off the alcohol, the residue dissolved in water, to which one-tenth its volume of strong hydrochloric acid has been added, and the volume made up to 50 cubic centimeters.

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* Bul. Soc. Chim., volume 50, page 625.

† Gunning, Scheibler's Neue Zeitschrift, 1888, XXI, 335.

The temperature is carried to 68° to invert the cane sugar, and after cooling, the solution is again polarized. The quantity of raffinose found by the formula is multiplied by 1.5 and gives thus the percentage of raffinose in the sugar. Methods of operation are also given for the analysis of raw sugars and molasses. The formula, with full details of method, is given on page 141.

ESTIMATION OF ASH IN SUGARS AND SIRUPS WITHOUT SULPHURIC ACID.*

Oxide of zinc is used, which has the following qualities to recommend it:

It is white, infusible, forms only a single oxide, is easily obtained in impalpable powder, is not hygroscopic, and it yields its oxygen as easily as the oxide of copper in the presence of organic matters and, in a measure indefinitely, because the zinc reduced to a metallic state is reoxidized immediately, and is susceptible therefore of furnishing a new quantity of oxygen to the substance until its complete combustion. The operation is conducted as follows:

In the case of sugar, 5 grams are weighed in a platinum dish, to which are added 0.05 gram oxide of zinc and a few drops of distilled water. The carbonizing is then carried on with due precaution over a Bunsen burner. The mass on melting absorbs evenly the oxide of zinc. After the carbonizing is completed the capsule is placed in a muffle, heated to low redness, and the incineration is completed after three-quarters of an hour or an hour at most. The ash is weighed and the 50 mg. of oxide of zinc subtracted. The capsule should be dried in a desiccator and weighed as rapidly as possible, since the carbonate of potash which is present is highly hygroscopic.

For sirups, the operation is carried on in the same manner, except sometimes it is preferable to weigh only 3 grams instead of 5. The capsules of platinum do not seem to suffer anything from the presence of the oxide of zinc, but porcelain dishes can be used instead.

ESTIMATION OF SUGAR IN THE BEET.†

It is stated that the amount of sugar in the beet, estimated by digestion in water, is, on an average, two-tenths per cent higher than by digestion in alcohol. Ninety-eight comparative determinations were made by the alcohol and water methods and the mean by alcohol polarization was 12.88 per cent and the mean by the water polarization 12.98 per cent. Careful deteriminations were also made in comparing the alcohol extraction with the cold water digestion on a very finely-divided beet pulp according to the Pellet method. The means of twenty-eight determinations were as follows: Alcohol extraction, 12.72 per cent; Pellet's cold water diffusion, 12.73 per cent; ordinary polarization in water, 12.81 per cent. It is recommended that alcohol extraction be used in all cases where scientific exactness is required.

INFLUENCE OF THE PRECIPITATE FORMED BY ACETATE OF LEAD UPON POLARIZATION.‡

Let S equal the weight of 100 cubic centimeters of juice; B, the weight of 10 cubic centimeters acetate of lead solution; N, the weight of the precipitate formed; F, the weight of the filtered liquid; then $S + B = N + F$. If F be replaced by the product of the volume V by the density d, we obtain $S + B = N + Vd$. If the volume of the precipitate be represented by v, we have the equation $V + v = 110$, whence $V = 110 - v$. From these equations the following one is derived:

$$v = \frac{110\,d + N - (B + S)}{d}.$$

From this formula is easily deduced the volume of the lead precipitate.

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* Lucien, Bulletin de L'Association des Chimistes, vol. 6, p. 356.

† Petermann, Zeitschrift des Vereins für die Rübenzucker-Industrie des Deutschen Reiches, 1889, p. 170.

‡ Ziegler, La Sucrerie Indigène, June, 1889, page 622.

Example.

Weight of 100 cubic centimeters of juice, plus 10 cubic centimeters of lead acetate = 118.509 grams = S + B. The specific gravity of the filtered liquid = 1.061 = *d*. The weight of the dried precipitate was found to be 3.005 = N, then by the formula above $v = 1.136$. It is thus seen that the lead precipitate occupies a little more than 1 per cent of the total volume.

ESTIMATION OF ASH IN SUGARS BY INCINERATION WITH BENZOIC ACID.*

To avoid the correction of one-tenth, as proposed by Scheibler, and one-fifth as proposed by Girard and Violette, when sugars are burned with H_2SO_4 Boyer suggests incineration with benzoic acid, as giving the real quantity of mineral matter without correction.

The benzoic acid is dissolved in alcohol of 90 per cent, 25 grams of the acid to 100 cubic centimeters of alcohol. 5 grams of the sugar are weighed in a capsule and moistened with 1 cubic centimeter H_2O. The capsule is heated slowly, in order to caramelize the sugar without carbonizing it; 2 cubic centimeters of the benzoic acid are next added and the capsule warmed until all the alcohol is evaporated; the temperature is then elevated until the sugar is converted into carbon. The decomposing benzoic acid produces abundant vapors which render the mass extremely porous, especially if a circular motion is imparted to the capsule. The slow heating is continued until all the benzoic acid is volatilized.

The carbon obtained is voluminous and of a brilliant black color. The incineration is accomplished in a muffle at a low red heat. The capsule should be weighed quickly when taken from the desiccator, in order to avoid the absorption of water by the alkaline carbonates. Benzoate of ammonia may be employed instead of benzoic acid, and the analyst should previously assure himself that neither the acid nor the ammonia salt leaves a residue on incineration. In addition to giving the mineral matters directly, this method permits the determination of their composition also, a matter of no small importance.

NOTES ON POLARIZED LIGHT.†

Experiments were made to determine what thickness of quartz gives the best sensitive tint for polarimetric work. Biot has said that the best tint is given by a piece of quartz 3.75 millimeters thick in a bright field. In most modern polarimeters the sensitive tint is given by a 7.5 millimeter quartz in a dark field. Experiments made with pieces of quartz 3.75, 11.25, and 7.5 millimeters in a dark field showed that the 3.75 millimeters was more sensitive than the 11.25 millimeters to small rotations, but the 7.5 millimeters seemed the best of the three. The sensitive tints of the German experimenters are decidedly redder than Biot's or those generally used in England.

In speaking of rotary polarization it is customary to say that the plane of polarization is rotated, but the author thinks it equally correct to say that the light itself is rotated. The use of bi-quartzes for rotation experiments was condemned, since it was found almost impossible to get them cut with such accuracy as to give a uniform tint, and if the light be slightly elliptically polarized considerable error may be introduced. The shadow method of polarimetry is preferred. The rotation power of liquids is believed to be due to some kind of skew symmetry possessed by the molecules, the average effect of which is observed.

NOTES ON THE ESTIMATION OF RAFFINOSE AND INVERT SUGAR.

According to Herzfeld and Meissl's directions it is possible to estimate saccharose in the presence of raffinose and invert sugar in the presence of saccharose. Accu-

* Comptes, rendus, 111.

† Prof. S. P. Thompson, Proceedings of Physical Society, Chemical News, vol. 59, No. 1541, p. 276.

rate results are, however, not obtained when all three sugars are present, as the rotation caused by invert sugar is not shown in Herzfeld's formula while the presence of raffinose causes an error in the direct polarization which is used in Meissl's table.

J. Wortmann recommends the following method with a somewhat complicated calculation (Zeitschr. 39, 767). The approximate amount of invert sugar present is determined with Fehling's solution prepared according to Soxhlet and the formula

$$N=\frac{Cu\ 47}{q},$$

when Cu is the copper found, q the weight of substance used, and 47 the average factor for Meissl's table. The value for N thus found is substituted in the following formulæ:

$$\text{I. per cent saccharose } S=\frac{0.9598\ P-1.85\ P'-0.277\ N}{1.5648}$$

$$\text{II. per cent raffinose } R=\frac{P-S+0.3103\ N}{1.85},$$

where P is the direct, P′ the indirect polarization (for whole normal weight). Therefore P—1.85 R is the total rotation caused by saccharose and invert sugar, and using this to find Meissl's factor, we can easily arrive at the actual per cent of invert sugar, J. This value J is then substituted for N in formulæ I and II and by calculation the exact quantity of saccharose and raffinose found.

The formulæ I and II are founded on the following basis, which was established by Herzfeld and others:

The factor of rotation of raffinose, with reference to saccharose, is $1.85=b$
The factor of rotation for inverted raffinose, with reference to saccharose, is $0.9593=c$ } at 20 C.
The factor of rotation for inverted saccharose, with reference to saccharose, is $0.3266=a$

26.048 grams saccharose after inversion, give a left-handed rotation of 32.66; since, however, 26.048 grams saccharose give 27.4191 grams invert sugar, this rotation, 32.66, is caused by 27.4191 grams invert sugar, and 26.048 grams invert sugar cause a rotation of 31.03, from which the rotatory factor for invert sugar is found to be $0.3103=d$.

By applying these values the following equations may be formed:

$$P=S+bR-dN. \quad (1)$$

$$P'=-aS+cR-dN. \quad (2)$$

$$R'=\frac{P-S+dN}{b} \quad (1)$$

$$P'=-aS+\frac{cP-cS+cdN}{b}-dN \quad (2)$$

$$bP'=-abS+cP-cS+cdN-bdN$$

$$bP'=-(ab+c)\ S+(cd-bd)\ N+cP$$

$$S=\frac{cP-bP'-bd-cdN}{ab+c}$$

$$R=\frac{P-S+dN}{b} \quad (1)$$

or, by substituting the values of a, b, c, and d, the above formulæ I and II.

Estimations made gave results closely agreeing with the known composition of the solutions.

THE DETERMINATION OF RAFFINOSE IN THE PRODUCTS OF THE BEET-ROOT MANUFACTURE, BY J. W. GUNNING.*

With regard to the directions for the estimation of raffinose published by the German customhouse, the author reports the results of investigations made during the last year in the official Dutch sugar laboratories, of which he is director. The accuracy of the method given in the official directions is limited to 0.33 per cent of raffinose, and no method is known which detects smaller amounts of raffinose with

* Z. f. anal. Chem., 1889, p. 45, from Chem. Zeitg. 1889, No. 6.

any accuracy. The author, however, considers the assumption that raffinose never occurs in quantities of less than 0.3 per cent to be wrong. The results obtained with products containing 3 per cent or more of raffinose show the accuracy of the German inversion method. Other mixtures may be brought within this percentage of raffinose by concentrating before actual analysis, and Scheibler applied the greater solubility of raffinose as compared with saccharose to accomplish this. Scheibler's method for the estimation of raffinose, however, gives too high results, and Lotmann's modification failed to correct the error. Ekenstein, the director of the royal laboratory at Amsterdam, has found the cause of the error in Scheibler's and Lotmann's method, and has thus shown a way of solving the problem. Methyl alcohol (similarly wood spirits, though in a much less degree) dissolves from the solid sugars not only the raffinose but also by far the most of the adherent molasses. Thus Scheibler obtained results which were too high. Lotmann's supposition that lead acetate precipitates from the methyl alcohol solution nothing influencing the rotation but raffinose, is incorrect. When the methyl alcohol is almost anhydrous the raffinose is completely precipitated, but also about ten times its weight of saccharose. Lotmann's and Scheibler's methods are, therefore, subject to the same error as regards the percentage of raffinose found. The accurate investigation of the influence which the gradual dilution of the methyl alcohol with water exerts upon the precipitates obtained with lead acetate opened a way for the accurate accomplishment of the purpose. The outlines for a raffinose estimation in sugar products are: Extraction with methyl alcohol (or wood spirits), partial removal of the solvent by heating, dilution with water, precipitation with lead acetate, and polarization of the filtrate before and after inversion.

In the Holland laboratories the Laurent shadow instrument is used (16.26 grams, normal weight). The following equations are applied in this case. Supposing: x = grams saccharose in 100 cubic centimeters of solution, y = grams raffinose, P polarization before inversion, p the same after inversion, and t = temperature.

$$\text{Then } 102\,x + 158.4\,y = 16.26\ \text{P}$$

$$-(44 - \tfrac{1}{2}\,t)\,x + (75 + \tfrac{1}{2}\,t)\,y = 16.26\,p$$

$$\text{Whence } y = 16.26\,\frac{(44 - \tfrac{1}{2}\,t)\,\text{P} - 102\,p}{158\,(44 - \tfrac{1}{2}\,t) + 102\,(75 + \tfrac{1}{2}\,t)}$$

The constants used are for a solution in 60 to 70 per cent alcohol, and have been determined in solutions of various concentration.

Following are the details for the method of estimating raffinose in sugar products:

(*a*) *For first products.*—One hundred grams are shaken in a stoppered narrow-necked 250 cubic centimeter flask with 150 cubic centimeters of commercial wood spirits which have been previously mixed with a few drops of potash-alum solution. The latter is added to neutralize the alkaline reaction of the sugar. The precipitated sulphates also carry down coloring matter. A 100 cubic centimeter flask is filled to the mark with the solution, 40 cubic centimeters removed by distillation, 20 cubic centimeters of water added, and lead acetate as long as a precipitate forms. A little moist aluminum hydrate is then added, the flask filled to the mark with water, well shaken, and the solution filtered rapidly and polarized. Fifty cubic centimeters of this filtrate are heated until all the methyl alcohol has been driven off, made up to 50 cubic centimeters with water, 5 cubic centimeters of hydrochloric acid (36 per cent HCl.) added, and heated for 10 minutes at 68° centigrade. Then it is cooled rapidly to 20° centigrade, and polarized in the 220 millimeter tube. The value y (raffinose) calculated from the equation when multiplied by 1.5 will give the percentage of raffinose.

Within 0.05 per cent of raffinose can be determined in sugars of high purity by this method. But to extract such small amounts rapidly some potassium acetate must be added to the solvent. With regard to the German report, the author notes that he does not know of any commercial article in Holland which would influence the custom-house method of examination.

(*b*) *For solid-after products.*—The raffinose in these is only dissolved very slowly and incompletely by methyl alcohol, and a modification of the method is therefore necessary. Thirty grams of raw sugar are treated in a graduated flask with 6 to 9 cubic centimeters of water and enough potash-alum solution to neutralize the alkalinity of the sugar. The sugar is then dissolved by heat and about 120 cubic centimeters of wood spirits added with continual shaking. After cooling it is made up to the mark with wood spirit, a little powdered sugar added, and the flask shaken frequently during one hour. After from 10 to 11 cubic centimeters of wood spirit have been added to correct for the volume of sugar separated, the liquid is filtered and the estimation continued as directed under (*a*). The value for raffinose found multiplied by 5 gives the percentage of raffinose. These estimations are accurate within 0.1 per cent of raffinose.

(*c*) *Molasses.*—On account of the solubility of molasses in methyl alcohol or wood spirit no concentration of the raffinose can take place, and the method is therefore very similar to the German inversion method. Twelve grams molasses are mixed in a 150 cubic centimeter flask with 12 grams water and the amount of potash-alum solution necessary for neutralization dissolved, and wood spirit added to the mark. It is then shaken, filtered, and the filtrate analyzed as under (*a*). The value found multiplied by 12.5 gives the percentage of raffinose present. In America the estimation of raffinose in raw sugars is made by a method only slightly varying from the German. (See Th. Breyer, Chemiker Ztg., 1889, 35, 499.)

SACCHARIMETRY—EXAMINATION OF SUGAR AND BEETS—VARIOUS METHODS.

While considering the various investigations concerning the invert sugar determination by Soldainis's reagent, which so far have not arrived at any constant results on account of the uncertain percentage of copper present, Striegler (Zeitschr., 39, 773) thought it would be of value to make a number of experiments for the purpose of finding a method by which the reagent could be prepared with a definite copper content. He beforehand studied the reactions which take place when the reagent is prepared according to Bodenbender and Scheller, and was thus enabled to elaborate a method by means of which a constant solution can be easily prepared. He has used this reagent in invert sugar determinations and has obtained results almost identical with those of Bodenbender and Scheller. In these experiments all the directions given by Degener and Schweitzer and later by Parcus (Jahresb., 28, 119–121) have been carefully followed so as to arrive at results absolutely free from error. Analyses of various quantities of the reagent prepared by the same method show:

(1) That a large amount, almost one-half, of the potassium bicarbonate used has been decomposed with the evolution of carbonic acid.

(2) That the amount of copper dissolved varies considerably between 131.1 and 159.7 mg. copper in 100 cubic centimeters; with regard to Preuss' figures even from 104 to 187 mg. copper in 100 cubic centimeters.

(3) That the quantity of copper carbonate dissolved is very low as compared with the quantity used. (Used a quantity corresponding to 0.727 gram copper, dissolved at the most 0.1597 gram copper in 100 cubic centimeters.)

Further experiments have proved that on dissolving the potassium bicarbonate in hot water a large amount is decomposed, and that in preparing the reagent more is used than can remain in solution at the ordinary temperature. It is therefore necessary after preparing the reagent to decompose the bicarbonate at least in part, so as to prevent any excess from crystallizing out. This can easily be accomplished by boiling.

Profiting by the results of further experiments, the author prepared a reagent of definite composition as follows:

An amount of copper sulphate corresponding to 0.1625 gram copper in 100 cubic centimeters was accurately weighed out, dissolved in cold water, made alkaline with soda lye, and the precipitate washed well. The usual amount of potassium bicar-

bonate was then added and the whole heated at 40° to 45° C. until the bicarbonate had dissolved and then at 60° until complete solution of the hydroxide of copper took place. This operation requires from one and a half to two hours, the preparation of larger quantities occupying a correspondingly larger amount of time. The solution was boiled some time to destroy the bicarbonate, cooled, and made up to the original volume.

Analyses show, as could be surmised beforehand, that this solution gives constant results; differences which could be ascribed to a varying carbonic acid content did not occur; we must naturally suppose that enough bicarbonate has been destroyed to prevent any crystallization.

The following method of preparation was finally adopted as serving the purpose:

To prepare 2 liters of the reagent, exactly 12.77 grams of pure, finely powdered copper sulphate were dissolved in cold water, precipitated with soda lye and the precipitate collected on a filter. A simple contrivance was used to facilitate washing. A flask holding about three-quarters of a liter was closed with a perforated stopper through which passed a glass tube about 6 to 7 centimeters long and 5 millimeters wide. The flask was inverted in such a manner over the funnel that the end of the tube was just below the level of the liquid in the filter. This arrangement is automatic and reliable. The washed hydrate was carefully transferred to a porcelain dish, removing the last particles from the filter with the wash bottle, mixed well with a glass rod, and then washed into a 2,500 cubic centimeter flask together with 597.7 grams potassium bicarbonate. Enough water was added to make the volume about 2,000 cubic centimeters. This was heated on the water bath to 45° C., frequently shaking, until the bicarbonate had dissolved, and then direct heat applied to dissolve the hydrate, not allowing the temperature to rise over 60° to 70° C. After complete solution the reagent is boiled for one to one and a half hours so as to decompose the bicarbonate, allowed to cool, transferred to a 2 liter flask, made up to the mark, and filtered. It is unnecessary to use a reflux condenser or to make up to 2 liters beforehand, as the escape of cabonic acid causes a concentration which must be corrected by the addition of water.

The solution in itself is stable, not even boiling causing decomposition. If, however, it is diluted with five times its volume of water, a bluish-green precipitate appears, which becomes black on boiling. This precipitate is therefore copper oxyhydrate, which is converted into black copper oxide on heating. This observation induced the author to examine the action of water on the usual Soldaini reagent. He found that when diluted with about twenty times its volume of water it also gave a precipitate of black oxide upon heating. This seems to indicate that the copper in Soldani's reagent is not present as carbonate, but rather as hydrate.

The behavior of basic carbonate of copper showed another way of preparing a constant reagent.

The basic carbonate prepared from 50 grams copper sulphate is heated for five or six hours with 300 grams potassium bicarbonate and about 700 cubic centimeters of water, the heat being kept at 45° C. as before until the bicarbonate has dissolved and then at 60° C. The solution is filtered and the excess of bicarbonate allowed to crystallize. The filtrate contained, in 100 cubic centimeters, 0.2882 grams copper and a quantity of potassium hydrate, corresponding to 36.7 grams potassium bicarbonate.

To prepare 1 liter of Soldaini's reagent (0.1625 gram Cu and 29.7 grams $HKCO_3$ in 100 cubic centimeters), 564 cubic centimeters of this solution are required, which contain 207 grams of the bicarbonate. It is therefore necessary to add 90 grams $HKCO_3$ or an equivalent amount of K_2CO_3, the use of the latter avoiding subsequent boiling for the purpose of destroying the excess of bicarbonate. A solution thus prepared could not be distinguished from another prepared by the first method. It depends altogether on the conditions whether one or the other should be preferred. If small quantities, for instance 2 liters, are to be prepared, the first is best applied; but if large quantities are required, as in manufacturing laboratories, where a steam bath is always at hand and the time is immaterial, then the last method is best followed.

The property of Soldaini's reagent to decompose when much diluted explained the varying results obtained in the first investigations upon its reduction by invert sugar. The conditions for this decomposition are fulfilled as soon as we begin to wash, especially if hot water is employed. To avoid this the author rejected the addition of water after boiling with the invert-sugar solution and substituted washing with a cold solution of potassium bicarbonate until all the copper had been removed, following with water to remove all the alkali.

The author then gives examples to show that results are obtained which agree with those of Bodenbender and Scheller.

Following are several contributions to the estimation of invert sugar by means of various copper solutions. Ettore Soldaini writes:*

"As I required a copper solution for the determination of glucose while making some special agricultural investigations, I asked myself whether I should use the popular Fehling's solution or should prefer (Arturo) Soldaini's reagent, which is prepared from copper sulphate and potassium bicarbonate and is a solution of copper carbonate in potassium bicarbonate.†

"On looking over the literature ‡ on this subject and considering the favorable manner in which the new solution had been received, as also the faults peculiar to Fehling's solution, I decided to use the former reagent; not, however, without being astonished at the high amount of copper directed for its preparation, which can not dissolve in a potassium bicarbonate solution of the given concentration, even when the modifications of Bodenbender and Scheller, which seem to enable a stronger solution, are followed. § In an actual experiment with the method of these authors, in which 40 grams of crystallized copper sulphate were dissolved, precipitated with 40 grams crystallized sodium carbonate, and washed to remove sulphates, the resulting basic carbonate would not dissolve completely after heating ten minutes on the water bath with a solution of 416 grams potassium bicarbonate, subsequent dilution to 1,400 cubic centimeters and again heating with reflux condenser for two hours. Upon filtering a blue liquid was obtained which was found to contain an amount of copper corresponding to 10.17 grams $CuSO_4 + 5H_2O$. For the Cu determination I employed Fresenius's method of precipitating in a platinum dish by means of zinc. By preparing the reagent several times and determining the copper I found the latter to vary from 1.856 to 1.845 grams, which latter figure would correspond to 7.25 grams $CuSO_4 + 5\ H_2O$ per liter.

"In other words, 10.15 grams $CuSO_4 + 5H_2O$ were sufficient to saturate the 1,400 cubic centimeters of reagent with copper under the conditions given. Soldaini's reagent can therefore be made of a constant strength by using this weight of $CuSO_4 + 5H_2O$ or less. If the usual method of preparation is followed, 11 grams should be used instead of 40 grams for 1,400 cubic centimeters.

"As these investigations show the impossibility of preparing a normal copper solution, I have adopted the one-tenth normal, dissolving 3.464 grams $CuSO_4 + 5H_2O$ and 297 grams $KHCO_3$ in 1,000 cubic centimeters of water, as I foresaw that this would give a much more delicate and stable reagent. It seemed unnecessary to precipitate the copper beforehand with sodium carbonate, and I prefer to add the solution of copper sulphate (or even the powdered salt) to the solution of potassium bicarbonate in a flask.

"Bodenbender and Scheller's directions concerning the washing of the copper carbonate may cause the assumption that the presence of sulphates exerts an influence on the delicacy of the reagent. Experiments have shown this to be not so, and that

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* Zeitsch., 39, 933.

† Gazzetta chimica italiana (1876), 6, 322; Berl. Ber. (1876), 9, 1126; Z. f. anal. chem. 16, 248.

‡ Degener u. Schweitzer, Zeitsch., 1886, 110; Bodenbender u. Scheller, Zeitsch., 1887, 145; Preuss, Zeitsch. 1888, 735.

§ Zeitsch. 1887, 147.

0.0005 gram glucose dissolved in 10 cubic centimeters can easily be detected when this is boiled for ten minutes with an equal volume of the reagent. The copper separates as intensely red suboxide. Under the above conditions less than the given amount of glucose can not be detected. If, however, the test is made in the manner which I will now give, then 0.00025 gram of glucose can easily be detected. The concentrated solution of the latter is mixed with just enough reagent to color it slightly and evaporated to dryness on the water-bath. If glucose is present, the porcelain dish will show a rose-colored residue, which in the absence of glucose would be bluish-green. Addition of water will show the color more distinctly. To avoid mistakes it is well to make a blank with the reagent similarly diluted.

"The quantitative determination with this reagent $\left(\frac{N}{10}\right)$ must be made as follows: Measure out 100 cubic centimeters (corresponding to 10 cubic centimeters of a solution containing 0.05 gram pure glucose), heat until boiling, and add the unknown solution slowly until all the copper is reduced. When the approximate number of cubic centimeters of the sugar solution required is thus determined, the final estimation is made by boiling 100 cubic centimeters of the reagent for five minutes in a 200 cubic centimeter flask, adding the required volume of sugar solution from a burette, boiling fifteen minutes, and filtering after the liquid has been cooled rapidly. The filtrate should contain neither glucose nor copper.

"This method gives such rapid and satisfactory results that I am induced to recommend the use of the $\frac{N}{10}$ copper solution."

A RAPID METHOD FOR THE ESTIMATION OF SUGAR WITH $\frac{N}{10}$ COPPER-ALKALI SOLUTION.*

"The determination of sugar with Fehling's solution would be accurate and rapid enough if the end of the reaction, that is, the complete decolorization of the alkaline copper solution, was easy to determine. The suspended copper suboxide makes this very difficult. To avoid this inconvenience and to make the determination more accurate and rapid, the author uses a definite amount of sugar solution, an excess of $\frac{N}{10}$ copper solution, and estimates the excess according to De Haen's method, with potassium iodide and sodium hyposulphite. The following solutions are required:

"(1) $\frac{N}{10}$ copper solution consisting of 24.95 grams pure copper sulphate, 140 grams sodium-potassium tartrate, 25 grams pure sodium hydrate, and sufficient water to make 1 liter.

"(2) $\frac{N}{10}$ solution of sodium hyposulphite, 24.8 grams per liter.

"(3) $\frac{N}{10}$ iodine solution, 12.7 grams per liter. The three solutions must correspond exactly and 1 cubic centimeter of the copper solution is equivalent to 0.0036 gram glucose.

"The estimation is made as follows:

"Fifty cubic centimeters of the copper solution are boiled in a porcelain dish and 10 cubic centimeters of a sugar solution added, which contains about 1 gram glucose in 1,000. The whole is heated for five minutes, made up to 100 cubic centimeters, and exactly 50 cubic centimeters filtered into a beaker. The blue liquid is made slightly acid, a slight excess of potassium iodide and some starch solution added, and the iodine estimated by means of the $\frac{N}{10}$ sodium hyposulphite solution. This iodine corresponds to the unreduced copper in the liquid, and the copper required

* J. E. Politis (Jour. de Pharm. et de Chim., 20, No. 2, July, 1889; Zeitsch., 39, 935).

by the glucose can be calculated by difference. The number of cubic centimeters of $\frac{N}{10}$ $Na_2S_2O_3$ solution required is deducted from 25 and the result will be the number of cubic centimeters of copper solution, which have been reduced by 5 cubic centimeters of the sugar solution.

"*Example.*—Fifty cubic centimeters $\frac{N}{10}$ copper solution were boiled with 10 cubic centimeters of diabetic urine which had been diluted to five times its volume and the estimation completed according to the above directions. Eleven cubic centimeters of $\frac{N}{10}$ $Na_2S_2O_3$ were required to completely decolorize the liquid; $25-11=14$ cubic centimeters of copper solution which had been reduced by one-half of the sugar solution; that is, 5 cubic centimeters of diluted or 1 cubic centimeter of the original urine. As 1 cubic centimeter of copper solution corresponds to 0.0036 gram glucose, 1 cubic centimeter of urine contained 0.0504, or 1 liter 50.4 gram glucose."

Scheller, in a preliminary notice, states that Soldaini's reagent can be made of a definite composition by dissolving 15.8 grams pure copper sulphate and 7.2 grams potassium hydrate respectively in 100 cubic centimeters of water, mixing, and adding to 1,700 cubic centimeters of a solution of 594 grams of potassium carbonate. It is then heated on the water bath until the precipitate has dissolved, and after cooling made up to 2,000 cubic centimeters. One cubic centimeter of this reagent contains 2 mg. of copper. It is said to be of a constant and stable composition.—(D. Zucker industrie, 1889, No. 14.)

E. Preuss (D. Zuckerindustrie, 1889, p. 1419; Zeitschr., 40, 118) notes the following concerning the quantitative determination of invert sugar with Soldaini's solution:

"In an earlier discussion on the reducing power of invert sugar I pointed out the necessity, in determining it with Soldaini's reagent, of always using a reducing liquid of constant composition; that is, having a certain percentage of copper and degree of alkalinity. The method of preparation outlined by me has now been so much improved by Scheller and Striegler that a solution is obtained by their process which seems to be well adapted for quantitative purposes. Scheller's method recommends itself by its simplicity. It consists in adding 15.8 grams copper sulphate to a hot solution of 594 grams potassium bicarbonate, and making up to 2,000 cubic centimeters, when the precipitate has been dissolved. Three solutions prepared in this manner showed the same specific gravity, 1.1789, a similar reducing power with regard to invert sugar solutions, and were very stable. As it is to be expected that the advantages which Soldaini's reagent possesses over Fehling's solution will cause its general adoption for the quantitative estimation of invert sugar, it will be of value to determine the exact reducing power of invert sugar with regard to this solution, especially as experiments so far made show it to be not exactly proportional to the quantity of invert sugar used. In the experiments described below I used Soxhlet's 1 per cent invert sugar solution, and made the reduction by heating 150 cubic centimeters of the copper solution by the direct flame and adding the invert sugar solution from a pipette.

"Upon boiling five minutes, 50 mg. invert sugar precipitated on an average 138 mg. copper; upon boiling ten minutes, 156 mg. copper; upon boiling fifteen minutes, 162 mg. copper; 75 mg. invert sugar on boiling five minutes, 190 mg. copper; 75 mg. invert sugar on boiling ten minutes, 215 mg. copper; 75 mg. invert sugar on boiling fifteen minutes, 231 mg. copper; 25 mg. invert sugar on boiling five minutes, 72 mg. copper; 25 mg. invert sugar on boiling ten minutes, 83 mg. copper; 25 mg. invert sugar on boiling fifteen minutes, 93 mg. copper; 40 mg. invert sugar on boiling five minutes, 112 mg. copper; 40 mg. invert sugar on boiling ten minutes, 127 mg. copper; 40 mg. invert sugar on boiling fifteen minutes, 138 mg. copper.

"This shows that a definite time of boiling must be observed in using Soldaini's reagent for quantitative determinations. As the separation of copper increases up to fifteen minutes boiling, and on the other hand such long boiling would render the

analysis cumbersome and the solution of copper suboxide possible, ten minutes were taken as the basis for the determination of the curve of reduction. Under these conditions

	Average.
I. 5 mg. invert sugar reduced..	19 mg. Cu.
II. 10 mg. invert sugar reduced..	34 mg. Cu.
III. 25 mg. invert sugar reduced..	83 mg. Cu.
IV. 40 mg. invert sugar reduced..	128 mg. Cu.
V. 50 mg. invert sugar reduced..	157 mg. Cu.
VI. 60 mg. invert sugar reduced..	184 mg. Cu.
VII. 70 mg. invert sugar reduced..	214 mg. Cu.

"Using these values the following proportion is calculated for the curve of reduction by the method of the least squares:

$$y = 2.2869 + 3.299\,x - 0.004101\,x_2,$$

where x represents the mg. invert sugar used, and y the corresponding amount of copper. By solving the quadratic equation the invert sugar can easily be calculated from the copper found. The following table has been prepared to facilitate this:

Mg. invert sugar.	Mg. cu.	Mg. invert sugar.	Mg. cu.	Mg. invert sugar.	Mg. cu.	Mg. invert sugar.	Mg. cu.
5	18.8	18	60.3	31	100.6	44	139.5
6	21.9	19	63.5	32	103.6	45	142.4
7	25.2	20	66.6	33	106.6	46	145.4
8	28.4	21	69.7	34	109.7	47	148.3
9	31.6	22	72.9	35	112.7	48	151.2
10	34.9	23	76.0	36	115.7	49	154.1
11	38.1	24	79.1	37	118.7	50	157.0
12	41.3	25	82.2	38	121.8	51	171.3
13	44.5	26	85.3	39	124.8	52	185.5
14	47.7	27	88.5	40	127.8	53	200.4
15	50.9	28	91.4	41	130.7	54	213.1
16	54.0	29	94.5	42	133.6	55	226.6
17	57.2	30	97.6	43	136.5	56	240.0

"The values of the table correspond satisfactorily to the quantities of copper found experimentally, as the following shows:

Mg. invert sugar.	Mg. copper.	
	Calculated.	*By experiment.*
5	18.8	19
10	34.9	34
25	82.2	83
40	127.8	128
50	157.0	157
60	185.5	184
70	213.1	214

In carrying out the estimations of invert sugar by Soldaini's reagent, we should closely follow the method of manipulation laid down, using for reduction an amount of polarized filtrate corresponding to 10 grams of substance. The filtration must not be too slow, and too great a dilution must be avoided, so that no subsequent formation of copper oxyhydrate or cuprous oxide takes place."

EXAMINATION OF SOME TABLE SIRUPS.*

The experimental station of the Austro-Hungarian Centralverein obtained several imported and a high grade domestic table sirup, and had them examined by the

* F. Strohmer, Oestreich, Zeitscher, 1888, 6.

methods elaborated by Herzfeldt and his followers, so as to obtain some knowledge concerning their nature. The following results were obtained:

	Imported table sirups.				Domestic sirup.
	I.	II.	III.	IV.	V.
Specific gravity at 17.5° C	1.4233	1.4173	1.4344	1.4309	1.4181
Degree Balling	81.10	80.22	82.74	82.23	80.33
Direct polarization	39.50	37.80	36.05	32.90	52.50
Polarization at 20° C. after inversion	−16.10	−17.0	−16.50	−16.60	−17.10
Reducing sugar determined as invert sugar, according to Preuss	25.50	21.56	28.34	21.67	0.47
Total solids*	74.13	71.04	74.03	74.28	77.55
Ash†	3.75	5.07	4.68	6.94	9.74

* By drying with sand at 100° C. in a vacuum.
† Sulphates after deducting one-tenth.

The following composition is calculated for the sirups from these analyses:

	I.	II.	III.	IV.	V.
Water	25.87	28.96	25.97	25.72	22.45
Cane sugar (Clerget)	41.91	41.31	39.60	37.30	52.45
Invert sugar	7.09	10.32	10.44	12.94	0.47
Optically inactive sugar	18.41	11.24	17.90	8.73	0.00
Ash	3.75	5.07	4.68	6.94	9.74
Organic matter not sugar, by difference	2.97	3.10	1.41	8.37	14.89
	100.00	100.00	100.00	100.00	100.00

Optically inactive sugar in this case is a mixture of glucose and invert sugar, in which the right-handed rotation of one is exactly equal to the left-handed rotation of the other. These analyses show that the domestic sirup is nothing more than a beet-sugar molasses, while the imported sirups are a better grade of colonial cane-sugar molasses. The taste and general appearance of the imported sirups showed them to be colonial molasses, while the domestic table sirup did not taste much better than common molasses.

On motion, the convention adjourned until Saturday morning at 9.30 o'clock.

THIRD DAY.

MORNING SESSION, SATURDAY.

The convention was called to order by the president at 9.30 o'clock.

Mr. Wiley said that at the time of adjournment on the preceding day he had finished the reading of his report upon sugar.

Mr. Caldwell moved that the methods for analysis of sugar products proposed by Mr. Wiley be adopted as the official methods for the coming year. Carried.

Mr. Myers presented the following report:

Mr. PRESIDENT: Your committee, appointed to consider and report upon the recommendations of our president in his address, beg leave to submit that they have carefully considered the recommendations made by him, and would respectfully recommend that—

First. We adopt potassium tetra-oxolate for the manufacture of the standard acid solution. (Referred to reporter on nitrogen.)

Second. (Consideration postponed.)

That in the determination of the citrate-soluble phosphoric acid all analysts be urged to adhere strictly to the scheme of analysis as to temperature, time, and manner of digestion, and that the filter pump be used in filtering.

REPORTERS ON FOODS AND FEEDING STUFFS.

Third. That the work of the reporters on "cattle foods," as now constituted, be divided, and that two reporters be appointed, one of whom shall consider methods of analysis, etc., relating to fodders, oil cake, and feed stuffs; the other to consider grains, mill products, and articles of human food not embraced under the work of other reporters already agreed upon.

Fourth. That a reporter be appointed to consider methods of ash analyses and soil analyses.

All of which is respectfully submitted by your committee.

JOHN A. MYERS,
R. C. KEDZIE,
H. W. WILEY.

Mr. Wiley moved that the report be accepted. Carried.

Mr. Wiley moved that discussion upon the recommendation in reference to phosphoric acid be postponed until the report of Mr. Burney upon that subject should be before the association. Carried.

By request of the president, Mr. Myers again read the first recommendation.

The president asked whether it was proposed to adopt potassium tetra-oxalate alone as a standardizer in testing the acid solution.

Mr. Myers said that such was the intention; it was to be taken as the standard.

Mr. Wiley said that this could not now be done without a reconsideration of the work already gone over. He moved that the recommendation in question be referred to the reporter on nitrogen, to be reported upon next year. Carried.

Mr. Myers again read the third recommendation.

Mr. Voorhees moved that the recommendation be adopted. Seconded.

Mr. Wiley moved that the recommendation be amended by striking out the words "reporter on cattle foods," and substituting in place thereof the words *reporters on foods and feeding stuffs*. He thought that the association was not warranted in distinguishing between human food and the food of other animals. The change suggested being made, he would be perfectly satisfied with the proposed division of labor between the reporters.

The motion was carried.

Mr. Huston said that the recommendation referred to a division of work already agreed upon. It was not clear to all what things each of the two reporters should handle, and some information ought to be given upon that point before the matter was passed.

Mr. Farrington suggested that a division might be made by separat-

ing the concentrated and coarse fodders, calling meal and oil cakes concentrated fodders, and hay, etc., coarse fodders.

Mr. Huston moved, as an amendment to the original motion, that the two reporters to be appointed should agree upon the division, their decision to be reported in the proceedings.

Mr. Caldwell said that the division would probably be determined by the methods of analysis. There were two classes of concentrated feeding stuffs, the milling product and the oil meals. As he understood, the proposed change was suggested by the large amount of farinaceous matter in food products, which required a somewhat different method of treatment. He did not quite like the classification contemplated; it did not divide the work equally, but gave to one reporter a very large amount of work, and left only the coarse fodders, straw, hay, etc., to the other. It might be better to include the oil meals and coarse fodders under one head and the grains and milling products under the other.

The president said that he understood that to be the recommendation of the committee in the original resolution.

Mr. Wiley said that Mr. Caldwell had expressed his own idea as to the division, that the starchy foods should go to one reporter and the foods in which the so-called nitrogen-free extract or other substances than starch formed the greater part of the digestible material should go to the other. The reporters could easily divide the stuffs by separating the starchy and non-starchy foods.

Mr. Myers said that the committee had the same idea. The process of fodder analysis made no provision for dealing with the difficulties arising from the presence of large amounts of starch in some of the materials, and the committee believed that the work should be divided in the manner stated by Messrs. Caldwell and Wiley.

Mr. Huston withdrew his proposed amendment, and the recommendation, as amended, was adopted.

Mr. Myers again read the fourth recommendation, and on motion of Mr. Caldwell the same was adopted.

The president stated that the business meeting of the association was now in order, and that the first business would be the election of officers for the ensuing year; he stated the qualifications of voters, as prescribed by the constitution, and appointed Mr. Voorhees as teller.

The following officers were elected by ballot:

President, Mr. G. C. Caldwell.

Vice-president, Mr. N. T. Lupton.

Secretary, Mr. H. W. Wiley.

Executive committee, Messrs. E. B. Voorhees and R. C. Kedzie.

Mr. Kedzie offered the following resolution:

Resolved, That the thanks of this association be tendered to the Smithsonian Institution for the use of this hall, and to the Department of Agriculture for the courtesies extended to this association, and the cordial interest shown in our transactions.

The resolution was adopted.

Mr. Robinson offered certain resolutions, which, after some discussion and amendment, were adopted in the following form:

Resolved, That a committee of three, of which Mr. Wiley shall be chairman, and the remaining members shall be named by the president of the association, be appointed to inquire into the desirability and feasibility of establishing a chemical laboratory at the Columbian Exposition to be held in Chicago in 1893, and to report at the next meeting of the association.

The president appointed as such committee Messrs. Wiley, Atwater, and Robinson.

Mr. Bowman offered the following resolution:

Resolved, That the reporters on the different subjects, such as potash, nitrogen, etc., be instructed to prepare an abstract of the changes made in the methods of analysis, and transmit a copy of the same to each member of the association as soon as possible after adjournment.

Mr. Atwater said that if the reporters would furnish him with brief abstracts of the changes made he would insert them in the coming number of the Experiment Station Record, which was nearly ready for the press.

The resolution was adopted.

The president said that Mr. de Ghequier, representing the German Potash Works, was present, and extended to the association an invitation to visit his office and examine the plans, photographs, etc., there exhibited, illustrating the work carried on by his company. He called upon Mr. de Ghequier to make a few remarks.

Mr. de Ghequier said that he felt under great obligation in being permitted to address the association, he being in no way connected with official chemical work. The work of the association was watched with keen interest from the other side of the water. He was especially indebted to Mr. Atwater, whose published writings contained the first impulse toward the now extensive use of potash salts in this country. In one of the first documents issued by the Office of Experiment Stations Mr. Atwater had stated that the difficulties of the newer stations were enhanced by the fact that nearly all the accumulated experience in regard to the subjects with which they had to deal was recorded only in foreign literature, and was, therefore, accessible only to a few, and had urged as a most important work the compilation of the main results of research in various special lines, to be published in forms conveniently suited to the use of American investigators. Acting upon this suggestion, the German Potash Works had intrusted to the speaker the compilation of results obtained in experimentation with potash salts. This compilation had been made and was submitted to Professor Wagner and other noted chemists before translation and publication in America. It was issued in pamplet form and had been widely circulated, its main object being to acquaint the public with the new position which the potash question had assumed in agricultural economy. Germany consumed in 1885 only 50,870 tons of kainit, while in the past year upwards

of 150,000 tons were required to supply the demand. These facts would serve to illustrate the practical results of rational application of potash salts in Germany.

The whole district north of Berlin had formerly been characterized by a sandy soil upon which grass would hardly grow, but was now covered with thriving orchards of peaches and other fruits. The change for the better had resulted from the application of potash salts, not alone, of course, but in combination with other fertilizing substances in which the soil may have been deficient. The conclusions to be drawn from these results seemed irresistible, and the German Potash Works had determined to present the facts to the United States so that the progressive spirit of this country might be prompted to investigate them and to ascertain to what extent the same means could be employed to produce similar effects in certain sections here. From what had already been done it seemed reasonable to believe that large areas of exhausted soils could be greatly benefitted by the application of these salts, which were not needed at all by rich soils not yet worked out. A scientific question in connection with the subject was met with in the influence exerted by potash salts upon plant growth. It had been found in Germany that by increasing the proportion of potash in fertilizers the plant became more apt to utilize the nitrogen and phosphoric acid inherent in the soil or furnished to it by artificial cultivation. The question thus raised was admitted to be important by Professor Wagner himself, who had declared his own inability to fully answer it without further study and research.

The mission intrusted to the speaker, he did not hesitate to say, had for its superior object the increase of consumption of potash salts in this country; but the German Potash Works stood upon the ground that this desired increase should not be brought about by advertisements soliciting the purchase of their products, but solely by their own merits as they should commend themselves, after experiment, to the agricultural colleges and experiment stations. This seemed to be the proper course, it being considered that none had the prosperity and advancement of agriculture nearer at heart than this association and the Association of American Agricultural Colleges and Experiment Stations, which would meet in November. Perhaps no words could more eloquently express the appreciation with which the German Potash Works regarded the efforts of these associations than the words used by Mr. Atwater on the excursion yesterday, to wit, that their progress, the decided improvement in their work, the enlargement of their scope, and the great interest and earnestness with which all workers had taken up their several lines of study and experiment rendered them the most important associations existing in the United States for the future prosperity of agricultural interests.

Mr. de Guequier thanked the association for the time extended to him, and renewed the invitation to visit the Washington office of the

German Potash Works and inspect the maps, plans, and photographs there on exhibition.

Mr. Burney presented the following:

REPORT ON PHOSPHORIC ACID.

By W. B. Burney.

Adopting the usual method of reporting on phosphoric acid, the subject will be presented in the following order: (1) Condensed abstracts of methods published during the year; (2) results of work done by members of the association and others; (3) recommendations for the next year.

ABSTRACTS.*

THE ESTIMATION OF PHOSPHORIC ACID BY AMMONIUM MOLYBDATE.†

For the titration of phosphoric acid by molybdate, the latter should be acidified with three to four molecular proportions of nitric acid to one of molybdic acid, while the phosphate solution is only slightly acidified. Under these conditions one molecular proportion of phosphoric anhydride is exactly precipitated by twenty-four of MoO_3. Ten grams of molybdic acid (or 12.262 grams of crystallized hexammonium heptamolybdate) is dissolved in an excess of dilute ammonia, the solution neutralized, further acidified with 15 grams nitric acid, and diluted to 1 liter. 24.3 to 24.5 cubic centimeters precipitate 0.01 gram P_2O_5.

For gravimetric determinations the author considers Finkener's method the best. The washed precipitate is dissolved in warm dilute ammonia, the solution evaporated until most of the ammonia is expelled, then mixed with an excess of nitric acid, evaporated and heated to complete decomposition of the ammonium nitrate, the final temperature being about 180°. The residue contains 3.753 per cent. P_2O_5.

If the precipitate has been washed with neutral ammonium nitrate, it may be titrated as follows: It is stirred up with cold water containing phenolphthalein and mixed with standard soda until it has completely dissolved and the liquid is red. It is then rapidly titrated back with nitric acid. One cubic centimeter $\frac{N}{10}$ soda = 0.00061739 gram P_2O_5.

ANALYSIS OF CONCENTRATED SUPERPHOSPHATES.‡

This superphosphate generally has from 4 to 5 per cent of P_2O_5 as ferric or aluminic phosphate which is insoluble in water but soluble in concentrated solutions of superphosphate. It is therefore important to use sufficient water in the first extraction, otherwise the soluble P_2O_5 will be reported too high. Take 1.5 grams of the superphosphate, place in a beaker and add a little water to soften and break up the lumps. Then make up to 90 cubic centimeters. Allow it to stand five minutes and filter off the supernatant liquid. To the residue add 90 cubic centimeters of water, stir, allow it to settle and filter. Treat the residue with 60 cubic centimeters of water, warm gently, bring upon the filter, and wash once with hot water.

CITRATE METHOD, PHOSPHORIC ACID DETERMINATION.§

The author supposes that the double phosphates with ammonium form soluble compounds with ammonium citrate, and that only the magnesium-ammonium phosphate

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* These abstracts were prepared by Mr. W. H. Krug, of the Chemical Division, Department of Agriculture.

† Hundeshagen, Fres.: Zeitsch. f. anal. Chem., 28, 165–172.

‡ Hughes, J.: Chem. News, 60, 91.

§ Reitmar, O.: Zeitsch. f. angew. Chem., 1889, 702–9, and 1890, 19–25.

is easily but never completely decomposed. To make this as complete as possible, more magnesium chloride than can combine with the ammonium citrate to form $MgNH_4C_6H_5O_7$ should be present so that this excess may act upon the compound $MgNH_4PO_4 + (NH_4)_3C_6H_5O_7$ which may have formed. Some $MgNH_4PO_4$, however, always remains in solution and causes a loss. When other bases (CaO, Fe_2O_3, Al_2O_3, MnO, FeO) are present, their phosphates are somewhat thrown down and cause an error. With CaO the error is largest. If the lime has been removed by oxalate or sulphuric acid, a loss of P_2O_5 may always be expected if we do not use at least twice the amount of magnesia mixture usually prescribed. Silica always contaminates the precipitate when present. The author considers the molybdenum method more accurate.

In addition to the above article the author notes the following: *

(1) Treatment of the substance with hydrochloric acid is objectionable, as the precipitate may contain considerable silica.

(2) Treatment with sulphuric acid reduces this error to about 1 mg. of silica.

(3) Even when an excess of ammonium citrate is present and only little CaO the precipitate contains from 1 to 2 mg. CaO as pyrophosphate.

(4) The presence of manganese exerts a similar influence.

(5) The error caused by Fe_2O_3 and Al_2O_3 in a sulphuric acid solution is very slight when little silica is present, even when large amounts of these oxides are present; they delay precipitation however.

(6) Small quantities of $Mg(OH)_2$ are always present; this error is slightest when the separation is made in a solution containing 2.5 per cent ammonia. In a nearly neutral solution and in the presence of alkaline salts the error is greatest.

(7) The phosphoric acid is always incompletely precipitated.

(8) In making a control-analysis by the molybdate method, the method of treating substances rich in silica must be regarded.

The average error according to the author is $\pm .128$ per cent, the — result where only small quantities of P_2O_5 are present.

With Thomas-slags and raw phosphates, the results are always too high.

THE USE OF PHOSPHORIC ACID OF ANIMAL OR MINERAL ORIGIN IN THE CULTIVATION OF THE SUGAR BEET.†

The results showed that no difference exists between the superphosphates of either animal or mineral origin.

ESTIMATION OF PHOSPHORIC ACID IN SLAGS. FORMATION OF TETRAHYDRATED FERRIC PHOSPHATE.‡

In eliminating by means of nitric acid the residual hydrochloric acid from slag, which had been treated with the latter reagent to remove silica, a probable source of error is shown by the author, in that a tetrahydrated ferric phosphate, $Fe_2(PO_4)_2 + 4\,H_2O$, is precipitated as a yellow granular powder. This differs from the normal ferric phosphate resulting from the precipitation of a ferric salt by disodium phosphate in not suffering dehydration at 110°.

ESTIMATION OF PHOSPHORIC ACID IN THE PRESENCE OF SILICA.§

The author proves by numerous experiments that phosphoric acid may be estimated in the presence of pretty large quantities of silica (solution of soluble glass acidified

* Reitmar, O.: Zeitsch. f. angew. Chem., 90, 196–210.

† Stoklasa, J.: Böhm. Zeitsch. f. Zuckerindustrie. 14, 137–142; Chem. Centralbl., 1890, I, 771.

‡ Arth, G.: Bull. Soc. Chim, (3) 2, 324–327; J. Chem. Soc., March, 1890, 292.

§ Preis, K.: Listy Chem., 13, 153, 154; J. Chem. Soc., July, 1890, 825.

with hydrochloric acid was employed) when the precipitate of ammonium phosphomolybdate is washed with pure cold water. As the liquid runs through the filter turbid at the end, double filters should be used.

Results of Work Done During the Year.

In answer to a circular letter sent out in the spring, forty-four replies were received, and thirty-seven chemists consented to participate in the work on phosphoric acid. It is to be regretted that many of these have failed to analyze the samples sent them. Early in May three samples were sent to each chemist consenting to do the work, and consisted as follows:

No. 1. A superphosphate.

No. 2. A complete fertilizer.

No. 3. A complete fertilizer containing cotton-seed meal and other substances difficult to oxidize.

These samples were prepared with the utmost care, and no pains were spared to insure absolute uniformity in the materials submitted for examination. The fertilizers had probably been made many months when they were collected for this work. They were first air-dried in thin layers for several days, and after grinding were passed through a sieve of forty meshes to the linear inch; the samples then stood for severa days more and were again mixed, first, in large jars, then by passing through a coarser sieve, and finally by hand on heavy paper, after which they were rapidly bottled and sealed.

From the specimens herewith submitted you may judge of the thoroughness of this work. It does not appear probable, therefore, that the differences in the analytical results presented in the following tables can be attributed to any lack of uniformity in the samples or to any dereliction on the part of your reporter. The results are tabulated in the order in which they were received, and are as follows:

No. 1.—*Superphosphate.*

	H_2O.	Soluble P_2O_5.	Reverted P_2O_5.	Available P_2O_5.	Insoluble P_2O_5.	Manipulation.	Total P_2O_5.
H. J. Patterson, experiment station, Maryland	6.10	9.18	3.72	12.90	4.42	h-l&c-p	[1]17.32
E. H. Farrington, experiment station, Illinois	6.42	9.16	3.37	12.53	5.00	hb-l-f	[2]17.53
C. L. Parsons, experiment station, New Hampshire	6.17	9.19	3.22	12.41	4.80	b-c-f	[1]17.21
F. W. Morse, experiment station, New Hampshire	5.99	8.98	2.95	11.93	5.09	b-c-f	[1]17.02
W. Wipprecht, experiment station Texas	[3]6.18	9.16	4.10	13.26	5.04	h-l-p	[1]18.30
D. O'Brine, experiment station, Colorado	7.07	9.29	2.13	11.42	5.83	h-l-p	1 & 2 17.25
Shepard Laboratory, Charleston, S. C	5.63	9.02	4.32	13.34	4.19	h-cl-p	[1]17.53
B. F. Finney, Department of Agriculture, Virginia	5.06	9.81	3.04	12.85	5.42	h-l-p	[1]18.27
R. H. Gaines, Department of Agriculture, Virginia	5.42	9.59	3.11	12.70	5.34	h-l-p	[1]18.04
Walker Bowman, experiment station, Virginia	5.87	9.58	3.32	12.90	4.80	h-c-p	[1]17.70
J. A. Fries, Pennsylvania State College	5.93	[4]9.48 [5]9.48	3.92	13.40	[4]4.63 [5]4.80	.....	18.03
H. B. McDonnell, Pennsylvania State College	6.11	[4]9.77 [5]9.86	3.11	12.88	[4]5.00 [5]4.99	.....	17.88
J. L. Hills, experiment station, Vermont	5.82	9.22	3.52	12.74	4.60	b-l-f	[9]17.34
B. O. White, experiment station, Vermont	.....	8.97	4.05	13.02	4.35	b-l-f	[9]17.37
F. B. Carpenter, experiment station, North Carolina	.....	9.31	3.85	13.16	[7]4.23	b-l-p	9, 1, & 2 17.39
B. W. Kilgore, experiment station, North Carolina	.....	9.39	3.25	12.64	[8]4.77	b-l-p	17.41
Aug. E. Knorr, United States Department of Agriculture	6.01	9.34	3.53	12.87	4.46	h-c-f	[9]17.33
A. L. Winton. R. S. Curtiss, experiment station, Connecticut	5.91	9.27	3.91	13.18	4.21	b-l-p	[10]17.39
H. R. Baldwin, experiment station, West Virginia	.....	9.02	3.22	12.24	4.72	b-c-f	16.96
R. C. Kedzie, experiment station, Michigan	[6]9.65	8.77	3.86	12.63	4.56	b-c	17.19
F. S. Shiver, Department of Agriculture, South Carolina	.....	8.90	4.66	13.56	4.22	b-c-f	[1]17.78
Average	6.21	9.26	.....	.....	4.75	.....	17.54

[1] $HNO_3 + HCl$.
[2] $HCl + KClO_3$.
[3] 98° C.
[4] Official method.
[5] Washed directly on filter.
[6] Dried in H at about 100°C.
[7] Solution in HNO^3.
[8] Solution in HCl.
[9] $Mg(NO_3)_2$ method.
[10] HCl.

No. 2.—*Complete fertilizer.*

	H_2O.	Soluble P_2O_5.	Reverted P_2O_5.	Available P_2O_5.	Insoluble P_2O_5.	Manipulation.	Total P_2O_5.
H. J. Patterson, experiment station, Maryland	9.27	6.52	3.81	10.33	0.87	h-l & c-p	[1]11.20
E. H. Farrington, experiment station, Illinois	10.61	6.12	3.65	9.77	1.43	h(b)-l-f	[2]11.20
C. L. Parsons, experiment station, New Hampshire	9.67	6.26	3.66	9.92	1.35	b-c-f	[1]11.27
F. W. Morse, experiment station, New Hampshire	9.59	6.29	3.71	10.00	1.39	b-c-f	[1]11.39
W. Wipprecht, experiment station, Texas	[3]9.71	5.80	4.29	10.09	1.26	h-l-p	11.35
S. T. Donaldson, Charleston, S. C	.....	6.03	4.34	10.37	1.07	f	[11]11.44
D. O'Brine, experiment station, Colorado	9.97	6.59	2.92	9.51	1.55	h-l-p	1 & 2 11.06
Shepard Laboratory, Charleston, S. C.	8.55	6.21	4.22	10.43	1.15	h-c-l-p	[1]11.58
B. F. Finney, Department of Agriculture, Virginia	7.50	6.87	3.22	10.09	2.00	h-l-p	[1]12.09
R. H. Gaines, Department of Agriculture, Virginia	7.44	6.72	3.25	9.97	2.15	h-l-p	[1]12.12
Walker Bowman, experiment station, Virginia	8.31	6.78	3.12	9.90	1.50	h-c-p	[1]11.40
J. A. Fries, Pennsylvania State College	8.60	[4]6.65 [5]6.60	4.01	10.66	[4]1.10 [5]1.23	.....	11.76
H. B. McDonnell, Pennsylvania State College	9.10	[4]6.72 [5]6.66	3.66	10.38	[4]1.29 [5]1.24	.....	11.67
J. L. Hills, experiment station, Vermont	9.25	6.54	3.29	9.83	1.27	b-l-f	[9]11.10
B. O. White, experiment station, Vermont	.....	6.40	3.33	9.73	1.23	b-l-f	[9]10.96
F. B. Carpenter, experiment station, North Carolina	.....	6.61	3.68	10.29	[7]1.05	b-l-p	1, 2, & 9 11.34
B. W. Kilgore, experiment station, North Carolina	.....	6.74	3.52	10.26	[8]1.05	b-l-p	1, 2, & 9 11.31
Aug. E. Knorr, United States Department of Agriculture	10.45	6.85	3.41	10.26	1.17	h-c-f	[9]11.43
A. L. Winton, R. S Curtiss, Connecticut Agricultural Experiment Station	9.32	6.57	3.57	10.14	1.15	b-l-p	[9]11.29
H. R. Baldwin, experiment station, West Virginia	.....	6.57	3.38	9.95	1.13	b-c-f	11.08
R. C. Kedzie, experiment station, Michigan	[9]12.55	5.97	4.15	10.12	1.16	b-c	11.28
F. S. Shiver, Department of Agriculture, South Carolina	.....	6.27	3.99	10.26	1.20	b-c-f	[10]11.46
Average	9.37	6.46	.....	.....	1.30	.....	11.40

b Balance.
c Coralline.
l Litmus.
f Filter.
p Pump.

[1] HNO_3+HCl.
[2] $HCl+KClO_3$.
[3] 98° C.
[4] Official method.
[5] Washed directly on filter.
[6] Dried in H at about 100° C.
[7] Solution in HNO_3.
[8] Solution in HCl.
[9] $Mg(NO_3)_2$ method.
[10] Solution in $H_2SO_4+KNO_3$.
[11] Ignited.

No. 3.—*Complete fertilizer, containing cotton-seed meal.*

	H_2O.	Soluble P_2O_5.	Reverted P_2O_5.	Available P_2O_5.	Insoluble P_2O_5.	Manipulation.	Total P_2O_5.
H. J. Patterson, experiment station, Maryland	5.45	6.32	2.77	9.09	2.68	h-l-c-p	[1]11.77
E. H. Farrington, experiment station, Illinois	8.10	6.12	2.51	8.63	3.27	h-b-l-f	[2]11.90
C. L. Parsons, experiment station, New Hampshire	5.56	6.35	2.61	8.96	2.88	b-c-f	[1]11.84
F. W. Morse, experiment station, New Hampshire	5.38	6.47	2.36	8.83	3.26	b-c-f	[1]12.09
W. P. Frost, Savannah, Ga	.....	6.41	3.13	9.54	2.70	.....	[9]12.24
S. T. Donaldson, Charleston, S. C	.....	5.83	3.96	9.79	2.58	f	[9]12.37
D. O'Brine, experiment station, Colorado	7.96	6.55	0.65	7.20	4.37	h-l-p	1 & 2 11.57
F. B. Dancy, Raleigh, N. C	.....	.....	.....	9.44	2.66	.....	[3]12.10
Shepard Laboratory, Charleston, S. C.	5.30	6.21	2.87	9.08	2.76	h-c-l-p	[1]11.84
B. F. Finney, Department of Agriculture, Virginia	4.42	7.01	2.86	9.87	3.53	h-l-p	[1]13.40
R. H. Gaines, Department of Agriculture, Virginia	4.38	6.65	2.91	9.56	3.49	h-l-p	[1]13.05
Walker Bowman, experiment station, Virginia	5.26	6.57	2.56	9.13	2.98	h-c-p	[1]12.11
J. A. Fries, Pennsylvania State College	5.48	{[4]6.56 / [5]6.55}	3.06	9.62	{[4]2.80 / [5]2.80}	.....	12.42
H. B. McDonnell, Pennsylvania State College	5.81	{[4]6.81 / [5]6.89}	2.28	9.09	{[4]3.03 / [5]3.12}	.....	12.12
J. L. Hills, experiment station, Vermont	4.99	6.32	2.98	9.30	2.92	b-l-f	[3]12.22
B. O. White, experiment station, Vermont	.....	6.27	3.15	9.42	2.90	b-l-f	[3]12.32
F. B. Carpenter, experiment station, North Carolina	.....	6.40	2.72	9.12	[6]2.73	b-l-p	1, 2, & 3 11.85
B. W. Kilgore, experiment station, North Carolina	.....	6.62	2.72	9.34	[7]2.90	b-l-p	1, 2, & 3 12.24
Aug. E. Knorr, United States Department of Agriculture	7.08	6.67	3.25	9.92	2.66	h-c-f	[3]12.58
A. L. Winton, R. S. Curtiss, Connecticut Agricultural Experiment Station	5.57	6.46	3.13	9.59	2.78	b-l-p	[3]12.37
H. R. Baldwin, experiment station, West Virginia	.....	6.50	3.42	9.92	2.31	b-c-f	12.23
R. C. Kedzie, experiment station, Michigan	[8]11.47	5.97	3.12	9.09	2.77	b-c	11.86
F. S. Shiver, Department of Agriculture, South Carolina	.....	6.16	3.46	9.62	2.78	b-c-f	12.40
Average	6.15	6.42	.....	.....	2.94	.....	12.21

b Balance.
c Coralline.
f Filter.
l Litmus.
p Pump.

[1] HNO_3 + HCl.
[2] HCl + $KClO_3$.
[3] Mg $(NO_3)_2$ method.
[4] Official method.
[5] Washed directly on filter.
[6] Solution in HNO_3.
[7] Solution in HCl.
[8] Dried in H at about 100° C.
[9] Ignited.

Averages.

	No. of determinations.	Average.	Highest.	Lowest	Difference.
Sample No. 1:					
Moisture	16	6.21	9.65	5.06	4.59
Soluble phosphoric acid	21	.....	9.81	8.77	1.04
Insoluble do.	21	.....	5.83	4.19	1.64
Total do.	21	17.54	18.30	16.96	1.34
Sample No. 2:					
Moisture	16	.....	12.55	7.44	5.11
Soluble phosphoric acid	22	.....	6.87	5.80	1.07
Insoluble do.	22	.....	2.15	0.87	1.28
Total do.	22	.....	12.12	10.96	1.16
Sample No 3:					
Moisture	15	.....	11.47	4.38	7.09
Soluble phosphoric acid	22	.....	7.01	5.83	1.18
Insoluble do.	23	.....	4.37	2.31	2.06
Total do.	23	.....	13.40	11.57	1.83

No. 1.—*Total P_2O_5.*

	Mg $(NO_3)_2$.	HNO_3 +HCl.	HCl+ $KClO_3$.	Ignition and HCl.	Ignition and HNO_3.	H_2SO_4+ KNO_3.
B. W. Kilgore, North Carolina	17.42 (HCl)	17.51	17.30	17.40	.....	.....
F. B. Carpenter, North Carolina	17.35 (HNO_3)	17.42	17.40	.....	17.09	....
F. S. Shiver, South Carolina	.....	17.81	.....	.....	.....	17.76
A. L. Winton, Connecticut	*17.40	.....	.....	.....	.....	17.52

* By HCl alone.

D. O'Brine states that "No. 1 will give different results according to the time it is treated by methods 2 and 3."

No. 2.—*Total P_2O_5.*

	Mg $(NO_3)_2$.	HNO_3 +HCl.	HCl+ $KClO_3$.	Ignition and HCl.	Ignition and HNO_3.	H_2SO_4+ KNO_3.
B. W. Kilgore, North Carolina	11.39 (HCl)	11.39	11.23	11.23	.....	.....
F. B. Carpenter, North Carolina	11.28 (HNO_3)	11.32	11.33	.....	11.41	....
F. S. Shiver, South Carolina	.....	.....	.....	.....	.....	{ 11.51 { 11.41
A. L. Winton, Connecticut	11.29	.....	.....	.....	.....	11.29

No. 3.—*Total P_2O_5.*

	Mg $(NO_3)_2$.	HNO_3+ HCl.	HCl+ $KClO_3$.	Ignition and HCl.	Ignition and HNO_3.	H_2SO_4+ KNO_3.
B. W. Kilgore, North Carolina	12.43 (HCl)	12.18	12.10	12.24	.....	.....
F. B. Carpenter, North Carolina	12.04 (HNO_3)	11.46	11.82	.....	12.06	....
F. B. Dancy, North Carolina	12.10 (HNO_3)	{ 11.49 { 11.56	11.78 11.74	{ 12.08	.....	11.69
H. B. McDonnell, Pennsylvania	.....	{ *12.03 { *12.15	{ §12.13	.....	.....	.....
Do	.....	{ †12.34 { †12.23	.....	.....	.....	.....
Do	.....	‡12.00	.....	.....	.....	.....
Do	.....	‖12.08	.....	.....	12.16	.....
C. L. Parsons, New Hampshire	.....	{ 11.51 { 11.48	.....	12.45 12.43	.....	.....
F. S. Shiver, South Carolina	.....	.....	.....	.....	.....	{ 12.43 { 12.37
A. L. Winton, Connecticut	12.37	.....	.....	.....	.....	12.34

* Thirty minutes. ‡ Forty-five minutes. ‖ Seventy-five minutes.
† Mo O_3 precipitate dark. § HNO_3+ $KClO_3$, and a little HCl after some time.

A study of the foregoing tables reveals discrepancies alike discouraging and inexplicable. It does not appear that we have made any advance since last year. That the methods employed in these determinations are trustworthy when properly executed follows from the fact that in the hands of a few experienced analysts the results are fairly within the limits of the working error. The fault, therefore, must be ascribed to the chemist, and is doubtless due to a lack of thoroughness, to a want of scrupulous attention to minute details in the processes of solution, precipitation, filtration, washing, etc. Thus, inspecting the tables, we see results which seem to be too high through incomplete washing of the precipitate of ammonium magnesium phosphate; total phosphoric acid too low, owing to incomplete oxidation in the process of solution; insoluble phosphoric acid too high or too low, because the ammonium citrate solution was too strong or too weak, acid or alkaline, and so on.

Comment in detail upon the analytical data seems unnecessary. A very few words will suffice. In the first place, the averages are given for what they are worth, and it is not claimed nor believed that in all cases they correctly represent the percentage of phosphoric acid present in the sample. The results on moisture are noteworthy, and seem to point to some grave oversight in the execution of the official method, if indeed the method was employed in all cases. It would be interesting to know how many of the chemists actually tested the steam closet to see that the temperature approximated 100° C.

With the possible exception of the soluble, the results on phosphoric acid can not as yet be regarded as satisfactory. So long as experienced analysts differ, in extreme cases, by 0.7 to 0.8 per cent, and from the average or probable truth by 0.3 to 0.4 per cent, it must be admitted that there is room for improvement. Now, if we omit from each table three or four of the analyses which seem to be extreme, there still remain a number which differ by the amounts above mentioned, Nor is this discrepancy confined to any one kind of phosphoric acid, but it is in varying degree true of all.

In the opinion of the reporter, the remedy for all this is to be sought not so much in the improvement of the methods of analysis, as in the increased care with which the details of the methods are executed after having been once adopted by this association.

Believing that changes in the official methods should be made with the greatest caution, and only for the best of reasons, the following recommendations are suggested after much hesitation:

(1) That in the preparation of the solution of water-soluble P_2O_5 the washing be continued until the filtrate measures 300 cubic centimeters.

(2) That in Chemical Bulletin No. 24, page 225, the second line from top of page be changed to read as follows: Filter the warm solution quickly through a 12½ centimeter plaited filter, wash twice with half-strength ammonium citrate solution and then with water of ordinary temperature.

(3) That in all cases of fertilizers containing cotton-seed meal, the solution for total phosphoric acid be prepared by the Mg $(NO_3)_2$ method.

(4) That the association advise, in the preparation of the solution of total phosphoric acid, the use of method No. 2 (30 cubic centimeters $HNO_3 + HCl$) for superphosphates and other samples free from organic matter; and the Mg $(NO_3)_2$ method for all cases in which organic matter is present.

It is further recommended that, with these changes, the present methods of determining phosphoric acid be continued, subject, of course, to modification by the association.

Mr. Burney said that an examination of the tables would show discrepancies which in many cases were very serious. In order to show that he was in no way personally responsible for those differences he had brought with him, and now exhibited, three of the samples just as they were prepared for distribution. As stated in the report, the samples were very carefully ground, air-dried, and passed through a forty-mesh sieve; they were then allowed to stand for some days to further air-dry, after which they were passed through a coarser sieve for the purpose of intimately mixing them. They were then mixed in large jars by rapid rotation and also by hand. He had omitted no precautions in the preparation of the samples, and those now presented would speak for themselves. They were drawn many months after the manufacture of the goods, so that it might be supposed that chemical changes had ceased to take place with any degree of rapidity. After a number of analyses were received he had seen by an inspection of the results that

further light was needed with regard to the methods of analysis. He therefore sent out a circular letter, asking certain questions, the answers to which would be found in the tables. He had hoped that the information obtained in answer to that circular would throw some light on the analytical results, but unfortunately it had not except as to the total phosphoric acid in sample No. 3. It would be found that the various methods had given different results. As the subjects were taken up in order he would have a word to say in regard to each recommendation.

Mr. Dancy presented the following paper:

ON THE DETERMINATION OF AVAILABLE PHOSPHORIC ACID IN FERTILIZERS CONTAINING COTTON-SEED MEAL.

By F. B. Dancy, A. B.

The term *available* phosphoric acid is used to denote the difference between the *total* phosphoric acid in a fertilizer and the *insoluble*. The *total* phosphoric acid is the entire amount of phosphoric acid, of whatever kind, that the fertilizer contains. The *insoluble* phosphoric acid is, as generally accepted, that phosphoric acid which is left after 2 grams of the fertilizer, ground to pass a sieve of approximately 20 meshes to the linear inch, have had the *soluble* phosphoric acid extracted with cold water and then been digested for thirty minutes, with agitation every five minutes, at 65° C., with 100 cubic centimeters of a strictly neutral solution of ammonium citrate of a specific gravity of 1.09 immediately after which digestion they have been thoroughly washed with cold water.

The *available*, then, being the difference between the *total* and the *insoluble*, it follows that *insolubles* being equal, the *available* varies exactly and directly as the *total*, and *totals* being equal, the *available* varies exactly, though inversely, as the *insoluble*.

The *total* is a definite and fixed quantity, and there should, therefore, be no material variation in its determination between the work of accurate analysts. Not so with the others. The *soluble*, *insoluble*, *reverted*, and *available* are not fixed and definite quantities. They are dependent on so many conditions of time, temperature, degree of fineness, quality and quantity of solvent, agitation, etc., that it is no matter of wonder that even skillful manipulators vary in their determination. They are the results of methods, and will vary according to the method or the manner of executing the details of the method. But, as has been remarked and as its name implies, the *total* is *all* the phosphoric acid in the material under examination, of whatever kind and in whatever shape or form. It is not what is gotten by a method but *what there is there*, and any method, therefore, that fails to reach any part or kind of it is not a method for *total* phosphoric acid. It is sometimes said that discrimination is impracticable, and that all fertilizers should be treated equally and alike. The position is untenable. It might as well be urged that in order not to discriminate, the plain soda-lime method for the determination of nitrogen should be used on all fertilizers, those containing nitrates as well as those containing organic nitrogen alone, when every one knows that it is inadequate in the presence of nitrates. So a *total* method which is adequate for some kinds of fertilizers but not for others can not be applied to all on the above ground or any other ground, without manifest injustice to those fertilizers for which the method is inadequate.

The Association of Official Agricultural Chemists in their official methods (Bulletin 24, United States Department of Agriculture), give three alternate methods of determining *total* phosphoric acid. There is no distinction made between them, no indication that either is better adapted than the other for any particular class of fertilizers. The presumption is that they are given as interchangeable and equally allowable for all classes of fertilizers, at the pleasure or option of the operator. It is

the purpose of this article to show that one of them, at least, is entirely inadequate for fertilizers that contain cotton-seed meal, and that any chemist who uses this method on such fertilizers is in almost certain danger of doing these fertilizers a great injustice. The method referred to is the second of the three given, namely: "Solution in 30 cubic centimeters of concentrated nitric acid with a small quantity of hydrochloric acid." The writer has not extended his investigation, except imperfectly, to the other two methods. It is only with this one, as applied to cotton-seed fertilizers, that this article has to do.

Cotton-seed fertilizers are comparatively unknown in the North. It seems, therefore, that the Southern members of the Association of Official Agricultural Chemists could not have been very wide awake to the interests of a class of fertilizer manufacturers peculiar to their own section of country when they failed to have attached to this method, at the time when it was adopted by their association as one of three alternate methods, the limitation "not applicable to fertilizers containing cotton-seed meal."

Cotton-seed meal is readily and entirely soluble in either "nitric acid with a small quantity of hydrochloric acid" or in nitric acid alone. *But such a solution does not give up its phosphoric acid to molybdic solution.* It would appear that certain nitro-organic compounds are formed which prevent the phosphoric acid in the solution from being yielded up to the molybdic precipitant. Whether this is effected by in some way rendering the menstruum a solvent for the phospho-molybdate of ammonia that ought to be formed, or, by holding the phosphoric acid in check, thus preventing such a combination, is not clear. But the fact remains. The attention of the writer was first forcibly directed to it when a sample of cotton-seed meal was submitted to him for a determination of the *available* phosphoric acid it contained. A nitric acid solution of 2 grams of it was made (using also a little hydrochloric acid), the solution being perfect, and a total phosphoric acid percentage of 0.51 found. A duplicate made in the same way yielded 0.54 per cent. Being convinced that there was much more phosphoric acid in the meal than this, and recalling that a short time previously a gentleman had remarked that a friend of his had found materially more phosphoric acid in the ash of cotton-seed meal than by acid solution, 2 grams of the meal were ignited to perfect ash, the ash dissolved in acid, and a percentage of 3.24 of *total* phosphoric acid found; a duplicate in the same manner yielded 3.20, though in this case the incineration was not quite so perfect, a little char being left. The true per cent of *total* phosphoric acid in the meal then was 3.24. A solution of 2 grams made by hydrochloric acid with chlorate of potash also failed by something more than half of getting the full amount. This yielded 1.45 per cent. Next 2 grams of the meal were taken, washed with cold water in exactly the same manner as when extracting *soluble* phosphoric acid from an ordinary fertilizer, then digested with citrate solution and again washed exactly as is done in the determination of *insoluble* phosphoric acid. The residue was ignited and the phosphoric acid determined. It was found to be 0.24 per cent. So not only did a cotton-seed meal which showed only half a per cent of *total* phosphoric acid to a nitric acid solution contain in reality $3\frac{1}{4}$ per cent, but 3 per cent of this $3\frac{1}{4}$ per cent was *available* by the methods of analysis.

A cotton-seed meal fertilizer may easily contain one-third cotton-seed meal, and, if the meal had the composition of that examined above, would owe 1 per cent of its *available* phosphoric acid to the meal. If, therefore, such a fertilizer were to be analyzed by the nitric acid method, it would theoretically show a shortage of nearly 1 per cent of *available* phosphoric acid (0.90 exactly). While none of the experiments herein given exhibit as great a disparity as this, some approximate it, and it is believed that a disparity fully equal to this is quite possible. Whether the entire disparity is always due to the retention of the phosphoric acid of the meal alone, or whether in some cases the meal, while holding some of the phosphoric acid of the phosphate in check gives up more of its own, or whether, in other cases, the phosphoric acid of the phosphate in precipitating carries more of the meal's phosphoric

acid down with it, than would otherwise go, and thus lessens the disparity, is not clear. I am inclined to think that new and fresh meal will exhibit this peculiarity in a greater degree than old meal, though of that I can not speak definitely. However that may be, there seems to be not much doubt that the disparity will be greater or less according to various conditions not well understood, and may vary from a third or a half of a per cent to even as much as 1 per cent.

Six fertilizers containing cotton-seed meal were chosen. They were not laboratory mixtures, but bona fide commercial fertilizers on sale in North Carolina. They will be distinguished as 56, 76, 77, 78, 110, and 57. In each the phosphoric acid was determined by dissolving 2 grams in nitric acid plus a little hydrochloric acid with protracted heating. This is designated in the table below as "acid solution." Then in each the phosphoric acid was determined by incinerating 2 grams and dissolving the ash in nitric acid. This is designated in the table as "incineration." Following are the results:

	Total phosphoric acid.					
	56.	76.	77.	78.	110.	57.
Incineration	10.04	9.77	9.16	9.93	10.07	9.97
Acid solution	9.49	9.13	8.66	9.25	9.56	9.95
Difference	.55	.64	.50	.68	.51	.02

No. 57 was an old cotton-seed meal fertilizer that had been carried over from last season. The meal had completely changed color to a dark brown, so that to the eye the fertilizer would never have been judged to be a cotton-seed fertilizer. In this one alone was there no difference in the results of the two methods.

It is believed that the disparity in all these cases is probably not so great as it should be; that is to say, that the incineration method as here used probably does not give the full content of phosphoric acid for this reason. The inferiority of the solvent power of nitric acid for phosphates to that of hydrochloric acid is well recognized. I believe that this inferiority is greater when the phosphate has been ignited. To test this an acid phosphate was chosen, of which 2 grams were dissolved in nitric acid and hydrochloric acid, and the total phosphoric acid found to be 14.56 per cent. Another 2 grams were then ignited for about the same length of time that it requires to incinerate 2 grams of a cotton-seed meal fertilizer to complete ash and then dissolved in nitric acid. The determinations were parallel, so that each received the same amount of heating with acid, which was protracted. In the case of the ignited phosphate undissolved portions were plainly manifest to the eye, and the percentage found was only 13.62. The undissolved portions were filtered out and readily yielded to hydrochloric acid, giving fulsome precipitate of phosphoric acid. Next, another 2 grams were ignited and dissolved in hydrochloric acid, when the full content of phosphoric acid was readily yielded. Hence, it is concluded that had hydrochloric acid been used to dissolve the six incinerated fertilizers employed in the above experiments higher percentages would in all probability have been found. Fusion would have furnished an absolutely certain means of arriving at the undoubted maximum content of phosphoric acid, but time was limited, and simple incineration was resorted to on account of expedition; and solution in nitric acid instead of hydrochloric acid was employed after incineration, because, as the results were to be compared, it was advisable to employ the same solvent power in each case.

In addition to the six experiments described above, attention is called to the following: Two samples of cotton-seed fertilizers were procured in which another chemist had made determinations of *total* phosphoric by the nitric acid method. His *totals* were 9.13 and 9.33. I found by incineration and solution in hydrochloric acid 9.85

and 10.13, a difference of 0.72 per cent and 0.80 per cent respectively. Taking his own determinations of *insoluble*, the *available* by his analysis was 0.72 per cent short in the first instance (7.40 per cent when it should have been 8.12 per cent), and 0.80 per cent short in the second instance (7.50 when it should have been 8.30 per cent). The disparity here is excessive, but the fault is not due to the chemist, but to the method. Being one of the alternate methods of the Association of Official Agricultural Chemists, he had no reason to doubt its adequacy.

Having looked at one side of the determination of *available* phosphoric acid in fertilizers containing cotton-seed meal, let us turn to the other, namely, the determination of *insoluble*. As almost the entire content of phosphoric acid in the meal has been shown to be available, it might be anticipated that there would not be likely to be much difference in the determination of *insoluble* whether the citrate-extracted residue is first incinerated or dissolved directly in acid. Such was found by experimentation to be the fact. In fact, in every case but one (and this was the same fertilizer that was the exception to the *total* rule, namely, the old one brought from the previous season) a slightly higher *insoluble* was found by dissolving in acid directly than after incineration.

The details of the two methods of determining the *insoluble* were these: After filtering from the citrate and thoroughly washing, the filter and contents were in the first instance incinerated and the ash dissolved in nitric acid (designated in the table below as "incineration"), and in the second instance the filter and contents were introduced directly into flasks and completely dissolved with nitric acid and a little hydrochloric acid (the "acid solution" of the table below). The samples used were the same as those used in the total experiments, with the exception of 110, which was not used.

	Insoluble phosphoric acid.				
	56.	76.	77.	78.	57
Incineration	0.84	1.80	0.86	0.87	1.59
Acid solution	1.00	1.91	1.28	1.05	1.42
Difference	.16	.11	.42	.18	.....

Whether the excess of *insoluble* by direct acid solution was due to mechanical loss in the incineration by the other method (which in these instances is not at all apprehended, though it is believed that care is necessary to with certainty guard against such loss) or whether, as is much more likely, it was due to imperfect solution of the ignited phosphate by nitric acid (a danger already pointed out), is not positively shown. But it should be remarked that in the case of 77, which is the case of greatest disparity, the undissolved portions were manifest to the eye, and it is the writer's conviction that had hydrochloric acid been used instead of nitric there would have been no material difference in the results of the two methods, either in these particular determinations, or in any other determinations. It is regarded as certain, therefore, that there will be found no material difference in the *insoluble* by whichever way determined.* This being true, the *available* will vary directly and exactly as the *total;* and, therefore, by just so much as a *total* is short on account of the inadequacy of the nitric acid method when used on cotton-seed meal fertilizers, by just so much will the *available* be short.

*Corroborated by determinations on phosphoric acid, reporter's sample No. 3, which showed:

	Per cent.
Per cent insoluble P_2O_5 by ignition and solution in HCl	2.67
Per cent insoluble P_2O_5 by dissolving filter and all in HC_3 and a little HCl (without igniting)	2.64

Now a few words as to what method *is* adequate, and a very few experimental determinations on this point, and the subject will for the present be laid aside. It is a matter of regret to the writer that the time was not at his disposal for more extended experimentation on the subject. Nevertheless he is none the less convinced, on account of the limited number of experiments here presented, of the truth of the point urged.

In order to compare the *total* as made by several different methods sample 110 was chosen. This sample was sent by a fertilizer company who took a fair sample of a large lot of goods at their factory, thoroughly mixed the sample and sent one-half to the writer and one-half to a chemist in another State. The *total* was determined first by fusing 2 grams of the fertilizer with a mixture of equal parts of carbonate of soda and nitrate of potash, as giving with certainty the maximum content, and furnishing a standard for comparison. It was then determined by incineration and solution in hydrochloric acid, by incineration and solution in nitric acid, by solution direct in hydrochloric acid with chlorate of potash, and lastly by solution direct in nitric acid and a little hydrochloric acid. Following are the results:

	Per cent.
Fusion	10.14
Incineration and solution in HCl	10.09
Incineration and solution in HNO_3	10.07
Solution direct in $HCl + KClO_3$	10.11
Solution direct in HNO_3 + little HCl	9.56

From the above it seems that in this case all the methods save the nitric acid methods were adequate, but it is not apprehended that this will hold good in all cases. For, while here incineration and solution in nitric acid sufficed, there is certainly the danger of imperfect solution already referred to; and while here also solution in hydrochloric acid with potassium chlorate sufficed, it has already been shown that this method failed to extract, from the meal alone, more than half its content of phosphoric acid.* Fusion is, of course, always adequate, but too time-consuming, if any other adequate method less so is at hand. It seems probable that incineration and solution in hydrochloric acid furnishes all that could be desired.†

It is in point to add that in this case the writer reported to the manufacturers a *total* of 10.11 per cent, this being an average of the first four determinations. The *insoluble* found by incineration and solution in hydrochloric acid was 1.47, making an *available* of 8.64. It is not known what method the chemist used to whom the other half of this sample was sent, but his *total* was 9.72, his *insoluble*, 1.50 and his *available*, therefore, 8.22. Note that the two *insolubles* are practically the same, and that, therefore, his *available* is less than the writer's by practically the same amount that the writer's *total* is greater than his.

The following results, obtained on sample No. 3 (containing cotton-seed meal) of the samples sent out by Dr. Burney, the reporter on phosphoric acid, for 1890, were submitted to that reporter, and are here appended as corroborative of the conclusions reached in the foregoing paper:

	Per cent.
I. Total P_2O_5, by evaporation with Mg $(NO_3)_2$, ignition and solution in HNO_3	12.10
II. Total P_2O_5, by simple incineration and solution in HCl	12.08
III. Total P_2O_5, by solution in $HCl + KClO_3$, two determinations $\left\{\begin{matrix}11.78\\11.74\end{matrix}\right\}$ averaged	11.76

* It did not suffice in sample No. 3 sent out by the reporter on phosphoric acid.

†Corroborated by determinations in sample No. 3 sent out by the reporter on phosphoric acid, which showed:

	Per cent.
Total P_2O_5 by ignition with Mg $(NO_3)_2$ and solution in HNO_3	12.10
Total P_2O_5 by simple ignition and solution in HCl	12.08

IV. Total P_2O_5, by solution in HNO_3 + little HCl, two determinations { 11.49 / 11.56 } averaged 11.53

I. Insoluble P_2O_5. After filtering from citrate solution and thoroughly washing, the filter and contents were ignited and dissolved in HCl. 2.67

II. Insoluble P_2O_5. After filtering from citrate solution and thoroughly washing, the filter and contents were put direct into a flask and dissolved in HNO_3 + little HCl 2.64

Mr. Gibson presented the following paper:

DIFFERENCES IN THE DETERMINATION OF REVERTED PHOSPHORIC ACID BY THE OFFICIAL METHOD OF ANALYSIS.

By Charles Gibson.

Having found it utterly impossible to make my analyses for the amounts of reverted phosphoric acid in several consignments of high-grade aluminic phosphate agree within several per cent with those of Messrs. Stillwell & Gladding, of New York, both of us using the official method, I proceeded to investigate by numerous experiments. The conclusions I have arrived at, and the reasons therefor, together with a few of the results I and others have obtained, I now propose to lay before this association.

When this material was first placed on the market my company, thinking perhaps we could use it profitably and advantageously in other respects in our factory, purchased a few consignments; and at the suggestion of the vendors we readily agreed to settle on the analyses of Messrs. Stillwell & Gladding, who were chemists of great eminence; and the fact of their using the official method of analysis contributed in no small degree to our ready assent. Their analyses of the different consignments, which they have since informed me were by the official method strictly as to time, temperature, etc., were checked by me, not using the official method however, but using the method which I use in controlling the work in the factory—the alkaline citrate method of Joulie—our results invariably agreeing to within one-tenth of 1 per cent. Goods were in due time made up with this material as one of the ingredients, and samples drawn and submitted to the chemists of the various States where they were likely to be sold. On the reports from the State chemists coming to hand we were surprised to find that they all, without a single exception, gave a very much lower percentage of available P_2O_5 than we had a right to expect, amounting to about 15 per cent on the ton of aluminic phosphate used.

Investigation proved that there had been no mistake in the weighing out of the materials. The proportions were found to be correct, and nothing of a retrograde nature could be discovered, at least with the Joulie method of analysis. But, in using the official method on the prepared goods, I obtained results which agreed completely with those of the State chemists. Evidently there was something wrong somewhere, and an analysis of a sample drawn from one of the consignments of aluminic phosphate (using the official method, instead of the alkaline method) indicated in which direction the trouble lay. This analysis gave results of about 15 per cent available P_2O_5 less than had been found by Messrs. Stillwell & Gladding. Repeated analyses with the same and other solutions failed to change this, and an examination by the official method showed the same state of things with regard to every consignment we had received. Through the kindness of two of the State chemists, the Hon. M. A. Scovell, of Kentucky, president of this association, and Prof. H. A. Huston, of Indiana, I have been able to verify the correctness of my results, at least as far as one consignment is concerned, as the following will show:

Stillwell & Gladding found 34.73 per cent available P_2O_5; total P_2O_5, 47.04 per cent.

Mr. Scovell, 20.31 per cent available P_2O_5; total P_2O_5, 44.25 per cent.

Professor Huston, 19.40 per cent available P_2O_5; total P_2O_5, 45.46 per cent.

My own, by official method, 19.70 per cent available P_2O_5; total P_2O_5, 46.7 per cent.

My own, by alkaline method, 34.74 per cent available P_2O_5; total P_2O_5, 47.0 per cent.

This matter thus assumed for us a serious aspect, for here we were both buying and selling on analytical results obtained by the official method, and yet, from a cause over which we had not the slightest control, we were subjected to a financial loss of very serious proportions, amounting to between $10 and $12 per ton of aluminic phosphate used.

Continuing the investigation with a view of finding whether or not this serious evil could be avoided, I found that infinitesimal variations in the preparation of the ammonia citrate solution of the official method very materially changed the results in the determinations of reverted P_2O_5 in this material. Although in the preparation and use of the ammonia citrate solution the directions as laid down in Bulletin No. 24, page 224, were followed with the utmost care, I was totally unable to prepare two solutions that would give anything like concordant results; and even with the same solution they were anything but uniform. The cause of this I found to be owing to very slight unavoidable variations in the composition of the ammonia citrate solution. I also found that the slightest inclination to acidity very largely affected the insolubility of this material. Now, from the mode of its preparation, it is evident that a perfectly neutral solution of citrate ammonia is practically unattainable, although the variations from neutrality must of necessity be of the minutest kind if proper care is used. These variations must either incline to alkalinity or acidity; but a little consideration would lead to the belief that, in almost every case (except where precautions are taken to insure the reverse), the inclination is to acidity.

I therefore prepared a solution of citrate of ammonia in the same manner as I conceived the majority of analysts, who did not know of the effect of this acidity, might prepare it. The directions in Bulletin No. 24, page 224, were followed with great care, and neutrality made by the addition of ammonia hydrate until the solution ceased to show acidity with blue litmus paper of great delicacy. Red litmus paper of great delicacy was also unaffected. I tried rosolic acid, but could do no better. We will call the solution A. Another solution, B, was made by adding ammonia hydrate to a portion of A until it showed a very faint alkalinity with delicate red litmus paper. The quantity of ammonia hydrate necessary to do this was about 1 cubic centimeter of a solution of the strength of 22° Baumé, to 1 liter of the A solution. I also prepared, with a view of obtaining a comparison of the two methods, a solution, C, according to the directions of M. H. Joulie, making it, as directed, strongly alkaline.

Before trying these solutions on the aluminic phosphate, I was curious to see what differences in effect, if any, they would produce on calcium phosphate. One gram of ground South Carolina rock containing 27 per cent P_2O_5 was taken in each experiment and digested without attempting to remove the small quantity of water-soluble (if indeed any were present). The official method was carried out strictly as to time, temperature, etc., with regard to A and B; and Joulie's directions in everything except time, which was only one-half hour instead of one hour with regard to C, no heat being applied in this case, it being digested at the temperature of the laboratory. The following results were obtained, in per cent of reverted P_2O_5:

	A.	B.	C.
	1.01	0.75	0.73
	0.90	0.73	0.74
	0.83	0.76	0.77
Mean,	0.913	0.746	0.746

Three experiments were now made in every respect the same as above, except that all were digested one hour, the time specified in Joulie's method, and the following results, in per cent of reverted P_2O_5 were obtained:

	A.	B.	C.
	1.85	0.787	0.73
	1.83	0.74	0.78
	1.86	0.76	0.77
Mean.	1.846	0.761	0.76

Five different portions of 1 gram each were now digested in C for four hours, and I obtained the following percentages of reverted P_2O_5: 0.71, 0.78, 0.79, 0.70, 0.75. Mean of the five: 0.746, or the same as B and C gave when the substance was digested only one-half hour.

There is great significance in the results thus obtained. The continuous dissolving action of the solution A is apparent; while both the B and C solutions cease to act as soon, apparently, as all the available P_2O_5 has been dissolved, which is within the first half hour; and an indefinite extension of the time of digesting, especially in the case of the C solution, seems to produce no further effect. Thus solutions B and C have been prepared, which, contrary to the generally accepted belief, will not go on continuously dissolving out P_2O_5 from calcium phosphate as long as any remains undissolved, provided enough time is allowed; and we have here (if, by further experiment, this is found by others to be true) a true measure of the availability of a phosphate, or at least a means of separating more sharply than we have hitherto been able to do soluble calcium phosphates from insoluble; and, with such a solution, which can be made by a very slight modification of the present official solution, the time element in the official method would cease to be an essential, as it is now, and would, in all probability, give much more accurate results, as well as conduce, more than anything else, to constancy and uniformity of results. From these experiments we perceive that a solution inclined to acidity, like solution A, tends, on calcium phosphate, to err on the side of too high a percentage of reverted phosphoric acid. The error is probably very small, but still that is the tendency. When, however, such a solution is used on aluminic phosphate, the reverse is the case to such an extent as to make the official method utterly worthless for the analysis of this material.

One gram of the aluminic phosphate containing 47 per cent P_2O_5, with 34.74 per cent available P_2O_5, according to Stillwell & Gladding, was digested in each of the solutions A, B, and C, strictly following as to time, temperature, etc., the official method with A and B; and Joulie's method, except as to time, which was one-half hour, instead of one hour, with C. The water-soluble, being insignificant in amount, was not removed before digesting. The following are the results obtained:

	A.	B.	C.
	19.80	31.24	26.18
	19.90	33.44	27.63
	19.63	30.31	26.92
Mean.	19.77	31.66	26.91

One gram of the material was now treated in every respect the same as in the last experiments, except that the digestion was one hour instead of one-half hour in all cases; and gave the following results, in per cent available P_2O_5:

	A.	B.	C.
	31.48	34.68	34.74
	32.11	34.79	34.72
	30.59	34.73	34.74
Mean,	31.39	34.73	34.73

It seems incredible that two solutions differing so very slightly in composition as do the solutions A and B should give such widely divergent results, the difference between the mean of the three results obtained by solution A and the mean of the three obtained by solution B, by digesting one-half hour, being no less than 11.89 per cent available P_2O_5. The lack of concord in the results obtained by each solution separately, together with the wide differences in the means of the results obtained from the three solutions, suggest the conclusion, however, that, in the case of each solution, the official time (one-half hour) was insufficient to dissolve the material.

By digesting one hour, concordant and uniform results are obtained by solutions B, and C. The results from A are still very much lower than B, although the difference is not so great as it was in the previous experiments. I found that the material was capable of being almost completely dissolved in all three solutions, if sufficient time was given.

Now, I am of the opinion that a critical examination of the ammonia citrate solutions of the majority of State and analytical chemists would reveal the fact that they are very close in composition to my solution A, in fact slightly inclined to acidity the fact of slight acidity in the solution affecting the insolubility of the aluminic phosphate not being generally known; while the chemists of the manufacturers, and perhaps a few others, being cognizant of this fact, have taken precautions to have their solutions incline to alkalinity rather than acidity. In some such way as this may we account for a considerable portion at least of the large difference in the amounts of available P_2O_5 found by Messrs. Stillwell and Gladding on the one hand, and the State chemists and myself on the other. The results obtained in these experiments, which are only a few out of many that I have made, warrant, I think, the following conclusions:

(1) That the official method, as it stands at present, is incapable of giving results on which an equitable adjustment of values—especially of aluminic phosphates—can be made, and it is urgently and imperatively necessary that either such modifications be made in it as will assure accuracy in all instances and under all circumstances, or that it be abandoned in favor of some other that may be depended upon.

(2) That it is possible to make such modifications in it as will enable analysts to obtain uniform and concordant results.

(3) That these modifications, if made in the direction which I will suggest, would conduce to greater accuracy and uniformity of results in the analysis of calcium phosphates.

With the view of making the comparison with the alkaline citrate method as accurate as possible, the amounts of available P_2O_5 obtained by it in these experiments and here given were determined as pyro-magnesium phosphate, checks being made by duplicates determined volumetrically. The agreement between the pyro-magnesium and volumetric determinations was very close, never varying more than 0.07 per cent. I have largely used this method during the last seven or eight years, and I have found it much more satisfactory than any other. The results obtained by it are reliable and uniform. It does not require that nicety and delicacy of manipulation and adjustment of solution that the official and other methods require, and there is therefore

less liability to error. It is more expeditious, the available being determined in one operation. The presence of organic matter does not impair the accuracy of the results either for total or available P_2O_5, and it is therefore unnecessary to destroy it. The results can be obtained either gravimetrically or volumetrically. The only drawback I find in the use of the method is that, in order to make sure of a complete precipitation of the ammonia magnesia phosphate, after adding magnesium mixture and vigorously agitating it, I find it necessary to let it stand over night. As a substitute for the present official method, if the association decides to abandon it, I think it might go farther and fare worse; and in any case it ought to be made an alternate method.

The present official method has been clearly demonstrated to be defective, erroneous, deceiving, and the cause of great financial loss, in one case at least; and this association, with whom alone rests the responsibility and to whom alone we must look for a remedy, will, I am sure, recognize the necessity, and make some immediate change that will not only restore confidence, but will conduce to uniformity and constancy of results, and insure accuracy and justice.

I am aware that capricious changes in official methods of analysis are to be deprecated, but in view of the facts here presented, I realize that this association must perforce take action in the premises. Therefore, with a full consideration of all the facts, and the conclusions fairly deducible from these experiments, and with a desire to aid the association in solving the problem with which it is now brought face to face, firmly believing that the changes here advocated will be a full and complete remedy for the defects in the official method which have been brought to light, I most respectfully submit the following suggestions:

(1) That instructions be given to add ammonia hydrate to the ammonia citrate solution, until a faint alkalinity is perceptible with red litmus paper.

(2) That the time of digesting be made one hour at 65° C.

(3) That Joulie's alkaline citrate method, with or without the modification of weighing as pyro-magnesium phosphate, be made an alternate method.

Mr. Huston said that he had done some further work in regard to the solubility of the so called reverted phosphoric acid in citrate of ammonia solution, an abstract of which here follows.

ACTION OF AMMONIC CITRATE ON HIGH-GRADE ALUMINIC PHOSPHATE.

By H. A. Huston.

In the latter part of July a sample of high-grade aluminic phosphate was submitted to me for analysis. The results desired were the amounts of total and of "available" phosphoric acid present. As the material was quite different from the ordinary fertilizer stock a series of experiments were made to determine the effects of varying the conditions used in the official method for available. Three methods for determining total phosphoric acid were used and gave closely agreeing results.

The material was stated to be anhydrous phosphate of aluminum, which had been calcined. It was found to contain 45.46 per cent of phosphoric acid and 7.25 per cent of silica. There was no soluble phosphoric acid present in the sample. The work on available phosphoric acid was made by using in all cases 100 cubic centimeters of the official citrate solution. In the fourth series solid citric acid and ammonic hydrate were added. The results appear in the following tables:

SERIES 1.—*Effect of increasing the time of digestion.*

[Amount taken, 2 grams. Temperature, 65° C.; 100 cubic centimeters citrate solution.]

Time of digestion.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
One-half hour	21.24	46.75
One hour	31.70	67.53
Two hours	36.92	81.10
Four hours	40.80	89.67
Six hours	41.00	90.11
Ten hours	42.70	93.85

SERIES 2.—*Effect of changing the temperature at which the digestion was conducted.*

[Amount taken, 2 grams; time, thirty minutes; 100 cubic centimeters citrate solution.]

Temperature.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
40° C	2.18	4.79
50° C	5.52	12.10
65° C	21.24	46.75
75° C	32.90	72.30
85° C	39.52	87.90

SERIES 3.—*Effect of changing the amount of phosphate taken.*

[Temperature, 65° C.; time, thirty minutes; 100 cubic centimeters citrate solution.]

Amount of phosphate taken.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
½ gram	16.80	36.9
1 gram	18.26	40.1
2 grams	21.24	46.7
3 grams	23.22	51.0
5 grams	24.66	54.2
10 grams	28.64	62.9

SERIES 4.—*Effect of making the citrate solution acid or alkaline.*

[Amount taken, 2 grams; time, thirty minutes; 100 cubic centimeters citrate solution.]

Amount of acid or alkali added to the solution.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
2 grams citric acid	17.21	37.21
1 gram citric acid	18.26	39.49
0.75 gram citric acid	17.84	38.58
0.50 gram citric acid	19.98	43.20
0.10 gram citric acid	21.08	45.60
0.05 gram citric acid	21.14	45.70
Neutral solution	21.32	46.10
Ammonia enough to neutralize 0.05 gram citric acid	23.44	50.70
Ammonia enough to neutralize 0.10 gram citric acid	24.38	52.70
Ammonia enough to neutralize 0.50 gram citric acid	26.02	56.30
Ammonia enough to neutralize 1.00 gram citric acid	30.78	66.60

The only set of the above results that seems to require any special comment is series 3, where the results are rather unexpected. The work in this direction will be continued in order to find out whether the peculiar effect is due to the fact that the digestion is stopped before the solution is complete, or whether a solution of aluminic phosphate in ammonic citrate really has a greater solvent power than the original solution of ammonic citrate.

The commercial importance of this matter will appear from the following: Suppose the high-grade phosphate is used in making up goods to the extent of one-fourth their weight. Then there should be 5.31 per cent of available derived from the aluminic phosphate. But if the results in series are correct there would appear on analysis only 4.20 per cent of available from this source.

The matter is also of considerable interest from a purely scientific standpoint.

The president said that in order to facilitate the disposition of the subject it would be well to take up first the recommendations of the reporter, debating such amendments and suggestions as should be offered thereon, and then consider any further amendments and other matters that might be presented in relation to the subject.

The first recommendation was again read, and it was moved that the same be adopted. Seconded.

Mr. McDonnell said that he thought the proposed change would make but a very slight difference in the amount dissolved. He had made a number of experiments on ordinary fertilizers, and had found that by washing up to 250 cubic centimeters and then 250 cubic centimeters more would only increase the soluble on the average probably 0.1 of 1 per cent, and 50 cubic centimeters would make a difference of only a few hundredths of a per cent.

Mr. Huston said that his experience was similar to that of Mr. McDonnell. He had never been able to detect any difference after the first 200 cubic centimeters, but perhaps he had washed with a smaller quantity of water than others used; he made as many washings as possible with as little water as possible; he thought that he did not use more than 2 or 3 cubic centimeters of water, and he got 30 washings without any trouble. The association was raising the solution at the rate of about 50 cubic centimeters a year, and that had better be stopped.

Mr. Burney said that he was strongly opposed to making unnecessary changes in methods. He would call attention to the fact that the official method now was not 250 cubic centimeters; the directions were "not less than 250 cubic centimeters." He had made it 300 cubic centimeters, but was perfectly willing to adopt 250 cubic centimeters as a fixed quantity; he thought that some fixed quantity should be adopted, and had supposed that 300 cubic centimeters would probably meet with the approval of most of the members of the association.

Mr. Gaines said that after washing with 200 cubic centimeters very little more was obtainable, scarcely 0.1 of 1 per cent. He moved that 250 cubic centimeters be adopted.

Mr. Voorhees said that a point which he wished to make was that on some high-grade superphosphates the washing made a considerable dif-

ference, and 200 and 300 cubic centimeters were not the same thing. He washed to 300 cubic centimeters, but there was no fixed limit prescribed.

Mr. Frear said that the unnecessary purchase of new apparatus was a matter that deserved consideration. He had a full stock of 250 cubic centimeter flasks and did not care to throw them away. In his laboratory the tests had been very carefully made under his own supervision, and with exact reference to the particular point now in question, and he had been unable to see any practical difference on quite a high grade of fertilizers. There seemed to be no necessity for adding labor without compensatory benefit, and he therefore preferred that the amount should be fixed at 250 cubic centimeters. He agreed with the reporter that it would be better to have a uniform amount, although he thought that in most cases the difference would not be large.

Mr. Kedzie said that it would only be necessary to strike out the words "not less than." The direction would then read (page 224): "wash with water until the filtrate measures 250 cubic centimeters."

The amendment was agreed to, and the recommendation as amended was adopted.

The second recommenation was again read and it was moved that the same be adopted. Seconded.

Mr. Voorhees asked what was the object of washing with citrate solution.

Mr. Burney said that he had, of course, expected serious opposition to the motion; for that he was fully prepared. On the other hand, he fully realized that no two filter pumps worked alike, and that to recommend one in the official method was to necessitate varying lengths of time for which the substance should be exposed to the action of the solvent; in other words, the method was one which caused the chemists to work under differing conditions, and that ought to be obviated if possible. So long as filter pumps were used the chemists could not hope to work alike. He had recommended the fluted filter because, so far as he could learn, it worked as rapidly as a filter pump. In the State laboratory where he worked the filter pumps were of very little use. The association could adopt a folded filter of such a kind that the filtration would take place at Washington in practically the same time as in South Carolina, and if the method recommended was equally convenient with that of the filter pump he saw no reason why the association should not adopt it, but every reason why it should.

Mr. Myers asked whether the filter pump used by Mr. Burney produced exhaustion.

Mr. Burney said that it did so but very slightly. For two years he had used with most satisfactory results a fluted filter which he exhibited. Several members of the association had used the proposed method on the samples, and spoke of it in the highest terms; he hoped that they would speak in regard to it now, as he felt that some change was very much needed.

A question had been asked concerning the washing with citrate solution. Every one knew that the suggestion came from Fresenius; it appeared in the original and in the translation. Fresenius recommended washing two or three times with half-strength ammonium citrate, and the object was to prevent the choking of the filter paper, a precautionary measure which was frequently necessary; the paper sometimes choked when water was added after draining off the citrate solution. Some determinations on the samples, using both methods, were as follows: The insoluble in No. 1, using the ammonium citrate half-strength, gave 4.21; without, it gave 4.23. No. 2, with ammonium citrate half-strength, 1.16; without, 1.24. No. 3, with ammonium citrate half-strength, 2.71; without, 2.85. In the last case the filter paper choked on the addition of water. Only one determination was made in each case.

Mr. Voorhees said that the determinations stated were within the limit of error in each case. He asked whether on the same sample, washing with citrate and with water, results within the limit of error could always be obtained.

Mr. Burney said that they could not. He saw no good reason for believing that the evils hinted at would arise. He thought that so careful a workman as Fresenius must have carefully settled the point before assuming the responsibility of recommending it in such a standard work as his unquestionably was, and as for himself, the figures just cited settled it to his entire satisfaction. It was undoubtedly true that the clogging of the filter paper would cause more trouble than could arise from the use of the half-strength citrate solution. The solution ran through with great rapidity, and acted but for a moment upon the residue remaining on the filter paper.

Mr. Voorhees said that filtering through folded paper was recommended last year, when he had suggested to the association that it be adopted, he having tried it for a whole year in the determination of phosphoric acid with very good results; the work had been continued in the same manner during the past year, and was found eminently satisfactory. For washing he had used the citrate solution, half-strength, for some time, and after a considerable number of determinations had concluded that the addition of citrate was not advantageous, the results without it being quite as good, and the filtration more rapid except on materials containing considerable oily matter, bones, for instance. On the whole he had concluded that it was better to use the water rather than the ammonium citrate solution.

Mr. Burney asked whether Mr. Voorhees meant to say that the filtration went on more rapidly without the use of half-strength ammonium citrate than with it.

Mr. Voorhees said that such had been his experience except on unusual samples of raw bone and others of similar character.

The president said that there were two important points in the recommendation, and suggested that a vote be first taken upon the question whether the fluted filter should or should not be used.

Mr. Gaines said that if Mr. Burney would use a Bunsen filter pump he could secure rapid filtrations and uniform results.

Mr. Burney said that a Bunsen pump required a well 40 feet deep or its equivalent. That could not easily be had.

Mr. Gascoyne said that a Richard pump would give much better results than a Bunsen pump. He should be sorry to have the association do away with the pump. His trouble occurred when he commenced to wash with cold water, particularly on fertilizers containing fish and cotton-seed meal. He thought that filtration was much more rapid when warm water was used for the washing; that gave him no trouble by clogging the filter, but passed right through.

Mr. Battle said that he was utterly opposed to the adoption of the fluted filter; he thought that ordinarily the pumps were strong enough, and that the washing of the fertilizer in the fluted paper would be very troublesome indeed; he had not tried it. In any event he thought that the change should not be made at this time; the association should at least postpone it for a year, and a trial could be had in the mean time.

Mr. Frear said that in his laboratory from ten to twelve determinations of the insoluble were made at one time; there were six filter pumps in the laboratory, and he had found it almost impossible to do the work so as to have the exposure the same on all the samples without great difficulty and danger of inequality by the use of the filter pump. He used the folded paper altogether, and generally two men had all they could do to keep the washing going on with twenty samples at one time without the use of the filter pump.

Mr. Huston said that he kept from ten to fifteen filter pumps running all the time, and did not believe that he could do without them. He made citrate-soluble in everything, and to him the pump was a necessity. He had never seen a filter which would let the first 100 cubic centimeters through inside of two or three hours in a citrate solution. His way was to decant and wash; he did not undertake to make a filtration on any single filter. His assistant said that he could do nothing without a pump; the washing would never be finished without it. He would suggest that the funnel of the filter pump be surrounded with hot water for the first 100 cubic centimeters.

The president said that in his laboratory, with the goods he had to deal with, it would be a very serious disadvantage to dispense with the filter pump.

The motion to adopt the second recommendation was lost.

The third recommendation was again read, and it was moved that the same be adopted. Seconded.

Mr. Huston moved that the recommendation be amended so as to apply to bone and bone meal as well as to cotton-seed meal.

Mr. Burney accepted the amendment.

Mr. Battle said that the recommendation seemed to him a very wise one. In his State the magnesium nitrate had worked well in almost all

fertilizers containing organic matter. He thought it might be advisable to extend the recommendation so as to cover all fertilizers containing organic matter.

Mr. McDonnell said that he did not think the change at all necessary. He would admit that he had but little experience in the use of the method, but he had tried it with the No. 3 sample and had difficulty in getting concordant results on the total acid; he got no higher result than with the ordinary method. He thought that to adopt the recommendation would be to return to the method of several years ago. The matter had been discussed in previous meetings.

Mr. Frear said that he saw no need of adopting the method, which presented some inconveniences, until it should be proven that the other methods were unsatisfactory. In the case of cotton-seed meal it did seem to be advantageous, but he was unwilling to see it extended to all fertilizers containing any kind of organic matter, and he should much prefer the adoption of the recommendation as originally submitted by the reporter, with the idea that the method be further and more carefully tested with reference to bone goods and goods containing other forms of organic matter during the coming year.

Mr. Gascoyne said that it was almost impossible to get the entire amount of phosphoric acid from cotton-seed meal with any of the wet processes; the only method by which that could be done was the magnesium nitrate method; but he saw no reason for extending that method to any other substance.

Mr. Dancy asked in what way it was objectionable to simply ignite the fertilizers and burn the organic matter to ash without the magnesium nitrate.

Mr. Gascoyne said that if insoluble phosphoric acid was present there would be danger of pyro-phosphate forming.

Mr. Dancy said that he had made tests in that regard; he had ignited acid phosphates for a long time and always found that the full content yielded to hydrochloric acid; he had never found that after ignition it could not be dissolved in concentrated hydrochloric acid.

Mr. Kedzie asked that the question be divided, the adoption of the method recommended for bone and for cotton-seed meal to be voted upon separately.

Mr. Burney said that lest the recommendation should not be adopted he wished to direct the attention of the association to the third table, an inspection of which would show but one or two cases where the phosphoric acid when determined by the nitro-hydrochloric method even reached the average, and he believed that the average was too low.

The motion to adopt the method recommended for fertilizers containing bone and bone meal was lost.

The motion to adopt the method recommended for fertilizers containing cotton-seed meal was carried.

The fourth recommendation was again read.

Mr. Burney said that the fourth recommendation was made as a mere matter of advice, and was not intended to be obligatory at all; it was hardly a recommendation, and no vote upon it was necessary; it would appear in the report as a suggestion.

The president said that in order to facilitate action the adoption of the method for the ensuing year would be considered section by section, reference being made to the report of the last meeting, pages 224, 225.

By several motions, which were carried, the methods prescribed in 1889 (page 224) for preparation of sample, determination of moisture, and water-soluble phosphoric acid were readopted without change.

It was moved that the method for citrate-insoluble phosphoric acid remain as it was last year (pages 224, 225). Seconded.

Mr. Williams, referring to the paper read by Mr. Gibson, said that at first sight it might appear that the high result of 34 per cent available phosphoric acid in the case stated was obtained only by himself (Mr. Williams) and Messrs. Stillwell & Gladding. On the contrary, a great number of official chemists, working strictly by the official method, got precisely the same result, which showed that there was something wrong in the method itself, and he thought he knew what that was. In December, 1886, and January, 1887, his firm sent samples to chemists in all parts of the country, and the following table would serve to show their agreements on available phosphoric acid:

	Per cent.
H. C. White	40.10
Charles W. Dabney	39.48
N. W. Lord	37.37
Stillwell & Gladding	40.16
F. A. Genth, Pennsylvania State Board of Agriculture	40.05

In February, 1889, the question again arose; certain parties who had bought his firm's goods had failed to get correct results, and samples were again sent to several chemists with the view of ascertaining whether the Keystone Chemical Company or the method was in error. On this particular sample his own analysis gave 33.52 per cent available phosphoric acid, and the following returns were received from other chemists:

	Per cent.
W. J. Gascoyne	32.88
Mr. Simon	31.03
Shepard Laboratory	26.36

A little later, in July, 1889, the question again coming up, he desired to make sure that he and Stillwell & Gladding, who usually acted as the company's arbitrators, so to speak, employed the official method, and a third sample was sent out, on which his own test gave 30.37 per

cent available phosphoric acid. On this sample the following returns were received:

	Per cent.
Stillwell & Gladding	30.60
Mr. Buck	30.87
W. J. Gascoyne	31.02
Shepard Laboratory	25.22
Mr. McCandless	32.35
Pringle Frost	30.25
H. C. White	31.27

Here were seven analyses all agreeing very closely, and only one dropping low. Hitherto the greatest discrepancies he had ever found amounted to 4 per cent, or thereabout, until Mr. Gibson's case, in which it amounted, he believed, to 15 per cent.

In studying out this question he had come to the conclusion that the slightest trace of acidity in the solution would cause the available phosphoric acid in the material to drop 3 or 4 per cent, and that the discrepancies were partially due to such slight traces of acidity in the so-called neutral citrate of ammonia solution. He had never succeeded in making such a solution, and others agreed with him in saying that to get an absolutely neutral ammonium citrate solution was impossible, and yet with the least degree of acidity in the mixture the results would go down enormously. If the question of slight acidity could be avoided fair agreements could be had.

In or before 1887 the official method for treating citrate insoluble goods was to place the flask in the bath at a temperature of 65° and digest at that temperature for thirty minutes. While that was the official method he had, comparatively speaking, no trouble with his goods, the discrepancies not exceeding from one-half to 1 per cent, and all the official chemists to whom the goods came agreeing fairly well. But in 1887 came the alteration that the flask was to be maintained simply in the bath, which was at a temperature of 65° for thirty minutes, which made fun for the official chemists, but not for the manufacturers. One trouble was that having a highly concentrated material, giving perhaps 33 or 35 per cent available phosphoric acid, but having at the same time only the same quantity of citrate of ammonia solvent as was used on other goods, the solvent had a great deal of work to do.

Again he had found that the question of time depended greatly on the quality of flask used. He had written to many chemists, inquiring how long a time it took for their citrate of ammonia in the flask to attain the temperature of 65°. Some said that they could get it up to that point in from three to four minutes; Stillwell & Gladding claimed that between four and five minutes was a long enough time; for his own part, he could not get it up to 65° in any flask he had tried under seven or eight minutes, and other chemists said that it took them nine or ten minutes. Stating it in that way it did not seem a great deal, but put in the converse form there was seen to be an enormous differ-

ence. So long as the directions read "hold it at 65° for thirty minutes" these discrepancies were of very little practical moment. On that point he had made a series of experiments, and with regard to the question of time his results differed widely from those shown by Mr. Huston. Having the bath at 65°, and reckoning the time from the moment of inserting the flask, the flask was held in the bath for thirty minutes, as directed in the official method, and the insolubles actually found were 12.26 per cent. Forty minutes (amounting in the circumstances under which he worked to about thirty-one minutes at 65°) gave 7.81 per cent insolubles; in fifty minutes they became 5.86 per cent, and in sixty minutes they only dropped to 5.31 per cent; fifty-five minutes gave 5.83 per cent, practically the same as at fifty minutes. These were not single experiments, but the mean of certainly five experiments in each case, so that to all intents and purposes the extraction seemed to stop in from fifty minutes to one hour, showing somewhat conclusively that simply being in a water bath at 65° for thirty minutes would not extract all that was soluble in the citrate of ammonia; there was not time enough, and the reaction was incomplete. If for any particular reason the citrate of ammonia could get at it easily and completely it would give a very high available phosphoric acid, but when it was given thirty minutes at 65° the discrepancies disappeared in a very marked degree.

Probably all had noticed that ammonium citrate solution made on a given day as neutral as possible would on the next day be distinctly acid—perhaps not in twenty-four hours, but certainly within a very short time; it would become acid sooner or later, and a very slight acidity was sufficient to make considerable difference on any mixture containing the goods of his company. So far as those goods were concerned he thought it would be strongly advisable, in order to get uniformity, to direct that the citrate of ammonium solution, instead of being neutral, should be faintly alkaline, and that the time of extraction should be made at least thirty minutes at 65°.*

Mr. Robinson said that his practice was to heat the ammonium citrate solution in a closed flask before using it, so that it was put in at the temperature of 65°. That was not the official method, but seemed to be really implied in it, and he had adopted it after experiencing much dif-

* In a communication received by the secretary subsequent to the meeting Mr. Williams requested that the following addition be made to his remarks:

I may add in further corroboration of my position that since making these remarks in August, 1890, another sample of our Keystone Concentrated Phosphate was analysed by several chemists, strictly by the official method, in October, 1890. The results are —

[Available phosphoric acid.]

	Per cent.
Messrs. Stillwell and Gladding	35.40
W. J. Gascoyne, Baltimore	33.77
Mr. Johnson, Connecticut	35.18
Mr. White, Athens	32.93
W. J. Williams, Philadelphia	35.09

ficulty with the ammonium citrate solution. As has been said, the solution would become acid. He had therefore, after making the solution as neutral as possible, added 3 or 4 cubic centimeters of coralline solution, and this gave a constant indication of the solution's exact condition; he could tell by looking at it whether or not it had become acid, and a drop or two of ammonia would correct the acidity. He got the best results by having the solution slightly alkaline, with the slightest purplish tinge or hint of a reaction.

Mr. Huston said he did not believe that the association could work on hints and tinges of alkalinity without being worse off than before. Moreover, according to his experience, the citrate solutions became alkaline rather than acid.

Mr. Gibson said that the paper he had read showed the results obtained by Mr. Huston on aluminic phosphate to be low, with a tendency to acidity. In all probability no phosphoric acid would have been dissolved after one hour had an alkaline solution been used. He would, therefore, move that the words "thirty minutes," in the first line on page 225, be stricken out, and the words *one hour* inserted in place thereof.

The motion was seconded.

Mr. Frear said that he would object very decidedly to such a change being made until it was better known what the facts really were, there being presented two sets of results which were not at all alike. He would further object to the adoption of any change resting upon facts relative to aluminic phosphate until their bearings upon calcium goods should be known. He fully realized the necessity for promptness of action, but the way proposed did not seem to be a safe one in which to go about the matter. He would be perfectly willing to have a committee appointed for immediate investigation of the subject, and was equally willing to abide by the decision of such a committee with reference to the particular matter under consideration after a careful examination as to the effects of a faintly alkaline solution as compared with the solution now prescribed in the method.

Mr. Kedzie said that the whole question needed, as Mr. Frear had said, some investigation. If he might be allowed to be a little out of order, he would say that chemists who had tested the neutrality of the solution by coralline would find that if it was neutral by coralline it was alkaline by litmus or cochineal. He thought it would be well to let the matter lie over for another year and obtain fuller information from the concurrent testimony of as large a number of chemists as possible before taking final action in regard to it. He moved that the whole subject of the time of digestion and the nature of the citrate solution be referred to the reporter on phosphoric acid, who should invite as many chemists as possible to investigate the matter and make returns thereon. Carried.

Mr. Burney said that it would be seen from the tables that a great

many of the chemists had not used the official method in neutralizing the ammonium citrate solution; numbers of them had used litmus paper which seemed to have been prepared by Squibb. He had repeatedly tested the matter of neutralization and had found that when ordinary litmus paper indicated that the solution was neutral the coraline gave an acid indication, and if to a solution made neutral by means of litmus paper a bit of either ammonium carbonate or sodium carbonate was added there would be an evolution of gas, clearly indicating that the solution was still acid. Therefore the litmus paper could not be trusted and coralline should be insisted upon.

Mr. Gascoyne moved that in the method for citrate insoluble phosphoric acid (page 225) the words *ordinary temperature* be stricken out and that the words "about the temperature of 65°" be inserted in the place thereof, so changing the method as to direct that the precipitate be washed with hot water instead of cold water. Carried; and on motion the method for citrate insoluble phosphoric acid (pages 224, 225), as amended, was adopted.

By several motions, which were carried, the methods prescribed in 1889 (page 225) for total phosphoric acid and citrate-soluble phosphoric acid were readopted without change.

The president said that the preparation of reagents necessarily followed the methods adopted, and required no separate action. Instructions to the reporter would now be in order.

Mr. Battle moved that the reporter be instructed to ask the analysts to compare different methods for total phosphoric acid as to their results on commercial fertilizers, especially those containing organic matter of any kind. Seconded.

Mr. Burney moved to amend the motion by including in the methods directed to be compared the one described by him last year, and set forth on page 98 of the bulletin.

Mr. Burney accepted the amendment and the motion was carried.

Mr. Gibson moved that the reporter be instructed to ask the chemists to compare the Joulie method in so far as to digest in a strong alkaline solution, cold, for one hour, and then either estimate the available phosphoric acid in the ammonium citrate solution as pyro-phosphate of magnesia or estimate the insoluble phosphoric acid by molybdenum and magnesia, as at present. Carried.

Mr. Gascoyne moved that the reporter be requested to send out as one of the samples either the aluminic phosphate or the phosphate manufactured by the Keystone Chemical Company. Carried.

On motion, the methods for determining phosphoric acid and moisture, as reported in 1889 (pages 224–226), and as amended, were adopted.

Mr. Wiley presented the following report:

REPORT OF COMMITTEE ON NATIONAL CHEMICAL SOCIETY.

GENTLEMEN: Your committee respectfully reports that it has conferred with a similar committee on the part of Section C of the A. A. A. S., and suggests that a committee of five be appointed by this association to coöperate with similar committees on the part of Section C, A. A. A. S., the Washington Chemical Society, and similar bodies, in calling a conference of chemists at some central point during the coming winter to consider the best means of organizing such a society.

H. W. WILEY.
W. C. STUBBS.

It was moved that the report be adopted. Carried.

Upon invitation by the president, Mr. Von Schweinitz exhibited some guinea pigs, and made the following statement:

In the interest of the Bureau of Animal Industry, Department of Agriculture, I have recently been making a study of the chemical products formed by the growth of the hog-cholera bacillus in artificial culture media. The bacteriological side of the question has, as most of you know, been very thoroughly worked out by Drs. Salmon and Smith, of the Bureau. After considerable trouble we succeeded in finding a medium that would yield the ptomaine in considerable quantity, and from these liquids, by adopting some modifications of Brieger's methods, I have succeeded in isolating an albuminoid body, which has been named *sucholo-albumin*, and an alkaloidal substance, or ptomaine, which I have called *sucholotoxin*.

We have gone a step further, and have succeeded in producing immunity in guinea pigs from hog cholera by previously injecting beneath the skin of the thigh different quantities of a solution of the *sucholo-albumin* or *sucholotoxin*, or both. The checks, pigs that were given the same sized dose of virus at the same time as the treated animals, invariably died, while the treated animals were but slightly affected by the virus, and recovered thoroughly, complete immunity being therefore produced.

The line of research is being continued; the experiments are being tried upon a large scale with guinea pigs and also upon hogs.

The guinea pigs which you see here are some of those which have been treated and then inoculated with hog cholera, and recovered; so you have before you a practical proof of the statements just made.

The president said that the report on fermented liquors, by Mr. Rising, was now in order.

Mr. Wiley said that as Mr. Rising had made a special trip to Europe to investigate the subject, and as he made no recommendations except that the method be continued as at present for next year, that he might have time to collate his report, and as he was reappointed, it might be well to simply read the communication by title and refer it to the printed proceedings.

Mr. Kedzie moved that Mr. Rising's communication be accepted and referred as suggested. Carried.

The communication here follows:

BERLIN, *August* 12, 1890.

Prof. H. W. WILEY,
Secretary A. O. A. C.:

DEAR SIR: Upon reaching this city I received a note from the president of the Association of Official Agricultural Chemists, containing the announcement that the meeting of the association will take place in August. I had counted upon having till September to finish my report, and expected to have been present at the meeting.

This is now impossible for several reasons. First, I have taken my passage from Liverpool for the 30th of August, and, second, I have business engagements which will detain me till that time whether I will or not. It is a matter of the greatest regret that I shall be obliged to forego the pleasure of meeting the members of the association at that time. It had not occurred to me that an earlier date would be set for the meeting, and consequently I am not able to give so complete a report as I had hoped to. The matter is made quite simple, because an agreement has practically been reached by German chemists which has my hearty indorsement. I have spent a good deal of time in getting the views of the leading chemists upon the important points connected with the various methods of analysis.

I spent some time in the municipal laboratory of Paris, met Mr. J. de Brevans, the chief chemist and discussed the subject with him. I visited Professor Fresenius and met his son, Dr. W. Fresenius and Dr. Borgemann. The meeting of the Bavarian chemists had taken place in May, so I could not attend it as I had hoped, but learned from those who were present the conclusions reached, and heard, "second hand," something of the discussion. I also visited Professor Rössler in Klosterneuburg bei Wien; Dr. Kayser, in Nuremburg, and Professor Hilger, in Erlangen, and others. Professor Hilger was kind enough to send me the resolutions of the Bavarian chemists, so that I think I am well informed in regard to methods in use here. I ought to say that I have been in close connection with my old teacher, Prof. von Hofmann, and Dr. Sell, now the chief chemist of the Gesundheits Amt. It will be of interest to the convention to hear that I have heard many appreciative words said about their work, by prominent chemists in Germany and elsewhere.

In regard to wine analysis I can only say that, by a general agreement, the conclusions adopted by the commission for the imperial health bureau (Gesundheits Amt) are universally adopted in Germany. The Bavarian chemists now work according to those methods. I will add the following suggestions to the paragraphs in last year's report.

Chemists here insist upon 15° instead of 25° as the better temperature for determining the specific gravity. Some were disposed to compromise on 20°, but I have found no one who was willing to adopt a higher temperature. It is very desirable to have all wine analyses made according to single standard, and then the results can be compared. I leave this, however, to the convention.

Extract evaporated to sirupy consistency on the water bath and then dried two and one-half hours at 100° in drying oven. (Drying to a constant loss is abandoned. My experience leads me most decidedly to this conclusion.)

In the glycerine determination the correction in (3) for the volatility of the glycerine is given up. According to experiments of Hehner it can be neglected.

The rest of the method can remain as in last year's report. I think perhaps it would be as well to omit what I added in regard to abnormal constituents. This is so special, and only one of many special methods to be used for abnormal wines, that my present judgment is that it would be better to omit it. The method of beer analysis, I think, may remain unchanged.

I wish to leave the report open to the suggestions and modifications of Drs. Crampton and Richards, based upon the analyses which they have made.

The interpretation to be given to the results of the chemical analysis of wines is a subject for special study and investigation; and this must be done for each country and district. It is only after we have ascertained by a large number of analyses what the constitution of the normal wine is that we can make comparisons.

In addition we have to fix limits for the amount of acid which may be contained in a good wine (including the amount of volatile acid). It may take some years yet to settle all of these points for the whole country, yet I look forward to a year of work which will go far toward establishing a standard or at least some approach toward a standard.

I have the honor to be, very truly, your reporter,

W. B. Rising.

The president nominated as a committee to confer with other committees in regard to a national chemical society Messrs. Wiley, Stubbs, Caldwell, Frear, and Nicholson.

It was moved that the executive committee be requested to appoint a time for next year's meeting following very closely or immediately the meeting of the American Association for the Advancement of Science, to be held in Washington if it be found feasible to do so. Carried.

On motion, adjourned.

OFFICERS, REPORTERS, AND COMMITTEES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS OF THE UNITED STATES FOR 1890–'91.

PRESIDENT.

Mr. G. C. CALDWELL, chemist of the New York Agricultural Experiment Station.

VICE PRESIDENT.

Mr. N. T. LUPTON, vice director and chemist of the Alabama Experiment Station, and official chemist of the Alabama State Department of Agriculture.

SECRETARY.

Mr. H. W. WILEY, chief chemist, United States Department of Agriculture.

EXECUTIVE COMMITTEE.

The PRESIDENT, VICE PRESIDENT, and SECRETARY, *ex-officio*,
Messrs. E. B. VOORHEES, of New Brunswick, N. J.,
R. C. KEDZIE, of Lansing, Mich.

REPORTERS.

Ash and soil.—Mr. R. C. Kedzie, of Lansing, Mich.
Dairy products.—Mr. W. W. Cooke, of Burlington, Vt.
Foods and feeding stuffs, high in carbohydrates (foods, grains, and their milling products, etc.). — Mr. Aug. E. Knorr, of Washington, D. C.
Foods and feeding stuffs, low in carbohydrates (coarse fodders, oil-seed residues, etc.).—Mr. Charles D. Woods, of Middletown, Conn.
Fermented liquors.—Mr. W. B. Rising, of Berkeley, Cal.
Nitrogen.—Mr. William Frear, of State College, Pa.
Phosphoric acid.—Mr. H. A. Huston, of La Fayette, Ind.
Potash.—Mr. H. B. Battle, of Raleigh, N. C.
Sugar.—Mr. William C. Stubbs, of Audubon Park, New Orleans, La.

COMMITTEES.

On National Chemical Society.—Messrs. H. W. Wiley, W. C. Stubbs, G. C. Caldwell, William Frear, and H. H. Nicholson.
On ways and means for securing more thorough chemical study of foods and feeding stuffs.—Messrs. W. O. Atwater, G. C. Caldwell, E. H. Jenkins, W. H. Jordan, and H. W. Wiley.
On chemical exhibit at the Chicago Columbian Exposition.—Messrs. H. W. Wiley, Norman Robinson, and W. O. Atwater.

CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

(1) This association shall be known as the Association of Official Agricultural Chemists of the United States. The objects shall be (1) to secure uniformity and accuracy of the methods, results, and modes of statements of analysis of fertilizers, soils, cattle foods,* dairy products, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

(2) Analytical chemists connected with the United States Department of Agriculture, or with any State or national agricultural experiment station or agricultural college, or with any State or national institution or body charged with official control of the materials named in section 1, shall alone be eligible to membership, and one such representative for each of these institutions or boards, when properly accredited, shall be entitled to vote in the association. Only such chemists as are connected with institutions exercising official fertilizer control shall vote on questions involving methods of analyzing fertilizers. Any person eligible to membership may become a member at any meeting of the association by presenting proper credentials and signing this constitution. All members of the association who lose their right to such membership by retiring from positions indicated as requisite for membership shall be entitled to become honorary members and to all privileges of membership save the right to hold office and vote. All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall have no vote in the association.

(3) The officers of the association shall consist of a president, vice-president, and secretary, who shall also officiate as treasurer; and these officers, together with two other members to be elected by the association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board whose members are eligible to membership, his office shall be considered vacant, and a successor may be appointed by the executive committee to continue in office till the annual meeting next following.

(4) There shall be appointed by the president, at the regular annual meeting, a reporter for each of the subjects to be considered by the association.

It shall be the duty of these reporters to prepare and distribute samples and standard reagents to members of the association and others desiring the same; to furnish blanks for tabulating analyses, and to present at the annual meeting the results of work done, discussion thereof, and recommendations of methods to be followed.

(5) The special duties of the officers of the association shall be further defined, when necessary, by the executive committee.

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* By a vote of the association, August 30, 1890, the subject of cattle foods was divided into two heads, namely, foods and feeding stuffs. It was understood by the latter of these divisions to include all fodders and feeding materials poor in starch and rich in fiber.

(6) The annual meeting of this association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

(7) Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any meeting, regular or special, seven enrolled members entitled to vote shall constitute a quorum for the transaction of business.

(8) The executive committee shall confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the association.

(9) All proposed alterations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by a vote of two-thirds of the members present and entitled to vote.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-'91.*

METHODS FOR THE DETERMINATION OF NITROGEN.

THE ABSOLUTE OR CUPRIC OXIDE METHOD.

[Applicable to all nitrogen determinations.]

The apparatus and reagents needed are as follows:

APPARATUS.

Combustion tube of best hard Bohemian glass, about 26 inches long and one-half inch internal diameter.

Azotometer of at least 100 cubic centimeters capacity, accurately calibrated.

Sprengel mercury air-pump.

Small paper scoop, easily made from stiff writing paper.

REAGENTS.

Cupric oxide (coarse).—Wire form; to be ignited and cooled before using.

Fine cupric oxide.—Prepared by pounding ordinary cupric oxide in mortar.

Metallic copper.—Granulated copper or fine copper gauze reduced and cooled in stream of hydrogen.

Sodium bicarbonate.—Free from organic matter.

Caustic potash solution.—Dissolve commercial stick potash in less than its weight of water so that crystals are deposited on cooling. When absorption of carbonic acid ceases to be prompt solution must be discarded.

LOADING TUBE.

Of ordinary commercial fertilizers take 1 to 2 grams for analysis. In the case of highly nitrogenic substances the amount to be taken must be regulated by the amount of nitrogen estimated to be present. Fill tube as follows: (1) about 2 inches of coarse cupric oxide. (2) Place on the small paper scoop enough of the fine cupric oxide to fill, after having been mixed with the substance to be analyzed, about 4 inches of the tube; pour on this the substance, rinsing watch glass with a little of the fine oxide, and mix thoroughly with spatula; pour into tube, rinsing the scoop with a little fine oxide. (3) About 12 inches of coarse cupric oxide. (4) About 3 inches of metallic copper. (5) About 2½ inches of coarse cupric oxide (anterior

*NOTE BY SECRETARY.—It was made the duty of the several reporters to prepare the methods of analysis as adopted by the association for editing by the secretary, the reporters being held responsible for the proper form of the text. All the reporters complied with this provision with the exception of Messrs. Jenkins and Burney. Mr. Jenkins did not attend the meeting. Mr. Burney did not forward any amended report of methods of analysis. The secretary has therefore changed the methods for dairy products and phosphoric acid as they appear to be ordered in the text of the proceedings.

layer). (6) Small plug of asbestos. (7) Eight-tenths to 1 gram of sodium bicarbonate. (8) Large, loose plug of asbestos; place tube in furnace, leaving about 1 inch of it projecting; connect with pump by rubber stopper smeared with glycerine, taking care to make connection perfectly tight.

OPERATION.

Exhaust air from tube by means of pump. When a vacuum has been obtained allow flow of mercury to continue, light gas under that part of the tube containing metallic copper, anterior layer of cupric oxide (see 5th above) and bicarbonate of soda. As soon as vacuum is destroyed and apparatus filled with carbonic acid gas, shut off the flow of mercury and at once introduce the delivery tube of the pump into the receiving arm of the azotometer, and just below the surface of the mercury seal of the azotometer, so that the escaping bubbles will pass into the air and not into the azotometer, thus avoiding the useless saturation of the caustic potash solution.

When the flow of carbonic acid has very nearly or completely ceased, pass the delivery tube down into the receiving arm so that the bubbles will escape into the azotometer. Light the jets under the 12-inch layer of oxide, heat gently for a few moments to drive out any moisture that may be present, and bring to red heat. Heat gradually mixture of substance and oxide, lighting one jet at a time. Avoid too rapid evolution of bubbles, which should be allowed to escape at rate of about one per second or a little faster.

When the jets under mixture have all been turned on light jets under layer of oxide at end of tube. When evolution of gas has ceased turn out all the lights except those under the metallic copper and anterior layer of oxide, and allow to cool for a few moments. Exhaust with pump and remove azotometer before flow of mercury is stopped. Break connection of tube with pump, stop flow of mercury, and extinguish lights. Allow azotometer to stand for at least an hour or cool with stream of water until permanent volume and temperature are reached.

Adjust accurately the level of the KOH solution in bulb to that in azotometer, note volume of gas, temperature, and height of barometer; make calculations as usual. The labor of calculation may be much diminished by the use of the tables prepared by Messrs. Battle and Dancy, of the North Carolina Experiment Station (Raleigh, N. C.).

The above details are, with some modifications, those given in the report of the Connecticut Station for 1879 (p. 124), which may be consulted for details of apparatus, should such details be desired.

THE KJELDAHL METHOD.

[Not applicable in presence of nitrates.]

APPARATUS AND REAGENTS.

(1) Standard hydrochloric acid whose absolute strength has been determined: (*a*) By precipitating with silver nitrate and weighing the silver chloride as described in Crook's Select Methods, page 571; (*b*) by potassium tetra-oxalate which has been purified by recrystallizing two or three times; (*c*) by determining the amount neutralized by the distillate from a weighed quantity of pure ammonium chloride boiled with an excess of sodium hydrate. Half normal acid, *i. e.*, containing 18.23 grams hydrochloric acid to the liter, is recommended. Cochineal or dimethyl-aniline orange to be used as the indicator in standardizing the acid.

(2) Standard ammonia whose strength, relative to the acid, has been accurately determined. One-tenth normal ammonia, *i. e.*, containing 0.7 gram ammonia to the liter, is recommended for acurate work.

(3) "C. P." Sulphuric acid, specific gravity 1.83, free from nitrates and also from

ammonia sulphate, which is sometimes added in the process of manufacture to destroy oxides of nitrogen. Eimer & Amend's "Strictly C. P." is good.

(4) Metallic mercury or mercuric oxide, HgO, prepared in the wet way. That prepared from mercury nitrate can not safely be used.

(5) Potassium permanganate tolerably finely pulverized.

(6) Granulated zinc, pumice stone, or one-half a gram of zinc dust to be added to the contents of the flasks in distillation, when found necessary in order to keep from bumping.

(7) A solution of 40 grams of commercial potassium sulphide in 1 liter of water.

(8) A saturated solution of sodium hydrate free from nitrates, which are sometimes added in the process of manufacture to destroy organic matter and improve the color of the product. That of the Greenbank Alkali Company is of good quality.

(9) Solution of cochineal prepared according to Fresenius's Quantitative Analysis, second American edition, page 679.

(10) Kjeldahl digestion flasks of hard, moderately thick, well-annealed glass. These flasks are about 9 inches long, with a round, pear-shaped bottom, having a maximum diameter of 2½ inches, and tapering out gradually in a long neck, which is three-fourths of an inch in diameter at the narrowest part, and flared a little at the edge. The total capacity is 225 to 250 cubic centimeters.

(11) Distillation flasks of ordinary shape, of 550 cubic centimeters capacity, or preferably flasks of the same capacity, of pear-shaped bottom, of well-annealed glass, for both digestion and distillation, and fitted with a rubber stopper and a bulb tube above to prevent the possibility of sodium hydrate being carried over mechanically during distillation. The bulbs are about 1½ inches in diameter, the tubes being the same diameter as the condenser and cut off obliquely at the lower end. This is adjusted to the tube of the condenser by a rubber tube.

(12) *A condenser.*—Several forms have been described, no one of which is equally convenient for all laboratories. The essential thing is that the tube which carries the steam to be condensed shall be of block-tin. The upper ends of the tin tubes should be bent so that the glass connections may have a slope toward the distilling flasks. All kinds of glass are decomposed by steam and ammonia vapor, and will give up alkali enough to impair accuracy. (See Kreussler and Henzold, Ber. Berichte, XVII, 34.) The condenser in use in the laboratory of the Connecticut Experiment Station, devised by Professor Johnson, consists of a copper tank, supported by a wooden frame, so that its bottom is 11 inches above the work-bench on which it stands. This tank is 16 inches high, 32 inches long, and 3 inches wide from front to back, widening above to 6 inches. It is provided with a water-supply tube, which goes to the bottom, and a larger overflow pipe above. The block-tin condensing tubes, whose external diameter is three-eighths of an inch, seven in number, enter the tank through holes in the front side of it near the top, above the level of the overflow, and pass down perpendicularly through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 1½ inches below the bottom of the tank, and are connected by short rubber tubes with glass bulb tubes of the usual shape, which dip into precipitating beakers or Erlenmeyer flasks of about 300 cubic centimeters capacity. The titration can be made directly in them. The distillation flasks are supported on a sheet-iron shelf, attached to the wooden frame that supports the tanks in front of the latter. Where each flask is to stand a circular hole is cut, with three projecting lips, which support the wire gauze or asbestos under the flask, and three other lips, which hold the flask in place and prevent its moving laterally out of place while distillation is going on. Below this sheet-iron shelf is a metal tube carrying seven Bunsen burners, each with a stop-cock like those of a gas-combustion furnace. These burners are of a larger diameter at the top, which prevents smoking when covered with fine gauze to prevent the flame from striking back.

(13) The stand for holding the digestion flasks consists of a pan of sheet-iron 29 inches long by 8 inches wide, on the front of which is fastened a shelf of sheet-iron as

long as the pan, 5 inches wide and 4 inches high. In this are cut six holes 1⅝ inches in diameter. At the back of the pan is a stout wire running lengthwise of the stand, 8 inches high, with a bend or depression opposite each hole in the shelf. The digestion flask rests with its lower part over a hole in the shelf and its neck in one of the depressions in the wire frame, which holds it securely in position. Heat is supplied by low Bunsen burners below the shelf. With a little care the naked flame can be applied directly to the flask without danger.

THE DETERMINATION.

(1) *The digestion.*—Seven-tenths to 2.8 grams of the substance to be analyzed, according to its proportion of nitrogen, is brought into a digestion flask with approximately 0.7 gram of mercuric oxide, or its equivalent in metallic mercury, and 20 cubic centimeters of sulphuric acid. The flask is placed on the frame above described, in an inclined position, and heated below the boiling point of the acid for from five to fifteen minutes, or until frothing has ceased. If the mixture froths badly, a small piece of paraffine may be added to prevent it. The heat is then raised until the acid boils briskly. No further attention is required till the contents of the flask have become a clear liquid, which is colorless, or at least has only a very pale straw color. The flask is then removed from the frame, held upright, and, while still hot, potassium permanganate is dropped in carefully and in small quantity at a time till, after shaking, the liquid remains of a green or purple color.

(2) *The distillation.*—After cooling, the contents of the flask are transferred to the distilling flask with about 200 cubic centimeters of water, and to this a few pieces of granulated zinc, pumice stone, or one-half gram of zinc dust when found necessary to keep the contents of the flask from bumping, and 25 cubic centimeters of potassium sulphide solution are added, shaking the flask to mix its contents. Next add 50 cubic centimeters of the soda solution or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distill until all ammonia has passed over into the standard acid. The first 150 cubic centimeters of the distillate will generally contain all of the ammonia. This operation usually requires from forty minutes to one hour and a half. The distillate is then titrated with standard ammonia.

The use of mercuric oxide in this operation greatly shortens the time necessary for digestion, which is rarely over an hour and a half in cases of substances most difficult to oxidize, and is more commonly less than an hour. In most cases the use of potassium permanganate is quite unnecessary, but it is believed that in exceptional cases it is required for complete oxidation, and in view of the uncertainty it is always used. Potassium sulphide removes all mercury from solution, and so prevents the formation of mercuro-ammonium compounds which are not completely decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen and prevents violent bumping. Previous to use the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates that are present which might otherwise escape notice.

KJELDAHL METHOD MODIFIED TO INCLUDE THE NITROGEN OF NITRATES.*

[Applicable to all fertilizers containing nitrates.]

Besides the reagents and apparatus given under the Kjeldahl method there will be needed—

(1) Zinc dust. This should be an impalpable powder; granulated zinc or zinc filings will not answer.

(2) Zinc sulphide.

(3) Commercial salicylic acid.

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*Described by Prof. M. A. Scovell.

THE DETERMINATION.

Bring from 0.7 to 1.4 grams of the substance to be analyzed into a Kjeldahl digesting flask, add to this 30 cubic centimeters of sulphuric acid containing 2 grams of salicylic acid, and shake thoroughly; then add *gradually* 2 grams of zinc dust, shaking the contents of the flask at the same time, or add to substance 30 cubic centimeters of sulphuric acid containing 1 gram of salicylic acid; then add direct 2 grams of zinc sulphide. Finally place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils briskly, and the boiling continued until white fumes no longer pour out of the flask. This requires about five or ten minutes. Add now approximately 0.7 gram mercuric oxide, or its equivalent in metallic mercury, and continue the boiling until the liquid in the flask is colorless, or nearly so. (In case the contents of the flask are likely to become solid before this point is reached, add 10 cubic centimeters more of sulphuric acid.) Complete the oxidation with a little permanganate of potash in the usual way, and proceed with the distillation as described in the Kjeldahl method. The reagents should be tested by blank experiments.

THE RUFFLE METHOD.

APPARATUS AND REAGENTS.

(1) Standard solutions and indicator the same as for the Kjeldahl method.

(2) A mixture of equal parts by weight of fine slaked lime and finely powdered crystallized sodium hyposulphite.

(3) A mixture of equal parts by weight of finely powdered granulated sugar and flowers of sulphur.

(4) Granulated soda lime, as described under the soda-lime method.

(5) Combustion tubes of hard Bohemian glass, 20 inches long and $\frac{1}{2}$ inch in diameter.

(6) Bulbed "U" tubes or Will's bulbs, as described under the soda-lime method.

PREPARATION.

(1) Clean and fill the U tube with 10 cubic centimeters of standard acid.

(2) Fit cork and glass connecting tube. Fill the tube as follows: (1) A loosely fitting plug of asbestos, previously ignited, and then 1 to $1\frac{1}{2}$ inches of the hyposulphite mixture. (2) The weighed portion of the substance to be analyzed is intimately mixed with from 5 to 10 grams of the sugar and sulphur mixture. (3) Pour on a piece of glazed paper, or porcelain mortar, a sufficient quantity of the hyposulphite mixture to fill about 10 inches of the tube; then add the substance to be analyzed, as previously prepared; mix carefully and pour into the tube; shake down the contents of the tube; rinse off the paper or mortar with a small quantity of the hyposulphite mixture and pour into the tube; then fill up with soda lime to within 2 inches of the end of the tube. (4) Place another plug of ignited asbestos at the end of the tube and close with a cork. (5) Hold the tube in a horizontal position, and tap on the table until there is a gas channel all along the top of the tube. Make connection with the U tube containing the acid, aspirate, and see that the apparatus is tight.

The combustion.—Place the prepared combustion tube in the furnace, letting the open end project a little so as not to burn the cork. Commence by heating the soda-lime portion until it is brought to a full red heat. Then turn on slowly jet after jet toward the outer end of the tube, so that the bubbles come off two or three a second. When the whole tube is red hot and the evolution of the gas has ceased and the liquid in the U tube begins to recede toward the furnace attach the aspirator to the other limb of the U tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U tube and wash the contents into a beaker or porcelain basin, add a few drops of the cochineal solution, and titrate.

THE SODA-LIME METHOD.

[Not applicable in presence of nitrates.]

APPARATUS AND REAGENTS.

(1) Standard solutions and indicator the same as for the Kjeldahl method.

(2) Granulated soda lime, fine enough to pass a 10-mesh sieve, and thoroughly dry.

(3) Fine soda lime, fine enough to pass a 20-mesh sieve, also thoroughly dry.

To prepare soda lime of the required fineness, the coarse granulated article of the trade may be ground until it will pass through a sieve of about ten-hundredths inch mesh. It is then sifted on a sieve of about twenty-hundredths inch mesh to separate the fine from the coarse. The two portions are then thoroughly dried in the air bath, or by heating in a porcelain dish or iron pan over a lamp, stirring constantly.

Excellent soda lime may be easily and cheaply prepared according to the directions of Professor Atwater (Am. Chem. Journal, vol. 9, p. 312), by slaking 2½ parts of quicklime with a strong solution of 1 part commercial caustic soda (such soda as is used in the Kjeldahl process), care being taken that there is enough water in the solution to slake the lime. The mixture is then dried and heated in an iron pot to incipient fusion, and when cold ground and sifted as above.

Instead of soda lime, Johnson's mixture of carbonate of soda and lime or slaked lime may be used.

Slaked lime may be granulated by mixing it with a little water to form a thick mass, which is dried in the water oven until hard and brittle. It is then ground and sifted as above. Slaked lime is much easier to work with than soda lime and gives excellent results, though it is probable that more of it should be used in proportion to the substance to be analyzed than is the case with soda lime.

(4) Asbestos which has been ignited and kept in a glass-stoppered bottle.

(5) Combustion tubes about 40 centimeters long and about 13 millimeters internal diameter drawn out to a point and closed at one end.

(6) Large-bulbed "U" tubes with glass stop-cock or Will's tubes with four bulbs.

THE DETERMINATION.

The substance to be analyzed should be powdered fine enough to pass through a sieve of 1 millimeter mesh: 0.7 to 1.4 grams, according to the amount of nitrogen present, is taken for the determination. Into the closed end of the combustion tube put a small loose plug of asbestos, and upon it about 4 centimeters of fine soda lime. In a porcelain dish or mortar mix the substance to be analyzed thoroughly, but quickly, with enough fine soda lime to fill about 16 centimeters of the tube, or about 40 times as much soda lime as substance, and put the mixture into the combustion tube as quickly as possible by means of a wide-necked funnel, rinsing out the dish and funnel with a little more fine soda lime, which is to be put in on top of the mixture. Fill the rest of the tube to about 5 centimeters of the end with a granulated lime, making it as compact as possible by tapping the tube gently while held in a nearly upright position during the filling. The layer of granulated soda-lime should be not less than 12 centimeters long. Lastly, put in a plug of asbestos about 2 centimeters long, pressed rather tightly, and wipe out the end of the tube, to free it from adhering soda lime.

Connect the tube by means of a well-fitting rubber stopper or cork with the "U" tube or Will's bulbs containing 10 cubic centimeters standard acid, and adjust it in the combustion furnace so that the end projects about 4 centimeters from the furnace, supporting the "U" tube or Will's bulb suitably. Heat the portion of the tube containing the granulated soda lime to moderate redness, and when this is attained extend the heat gradually through the portion containing the substance so as to keep up a moderate and regular flow of gases through the bulbs, maintaining the heat of

the first part until the whole tube is heated uniformly to the same degree. Keep up the heat until gases have ceased bubbling through the acid in the bulbs and the mixture of substance and soda lime has become white or nearly so, which shows that the combustion is finished. The combustion should occupy about three-quarters of an hour, or not more than one hour. Remove the heat, and when the tube has cooled below redness break off the closed tip and aspirate air slowly through the apparatus for two or three minutes to bring all the ammonia into the acid. Disconnect, wash the acid into a beaker or flask, and titrate with the standard alkali.

During the combustion the end of the tube projecting from the furnace must be kept heated sufficiently to prevent the condensation of moisture, yet not enough to char the stopper. The heat may be regulated by a shield of tin slipped over the projecting end of the combustion tube.

It is found very advantageous to attach a Bunsen valve to the exit tube, allowing the evolved gases to pass out freely, but preventing a violent "sucking back" in case of a sudden condensation of steam in the bulbs.

METHODS OF ANALYSIS OF DAIRY PRODUCTS.

BUTTER.

MICROSCOPIC EXAMINATION.

Place a small portion of the fresh sample taken from the inside of the mass on a slide, add a drop of pure sweet oil, cover with gentle pressure, and examine with a one-half to one-eighth inch objective for crystals of lard, etc.

Examine same specimen with polarized light and selenite plate without the use of oil.

Pure fresh butter will neither show crystals nor a parti-colored field with selenite. Other fats melted and cooled and mixed with butter will usually present crystals and variegated colors with the selenite plate.

For further microscopic study dissolve 4 or 5 cubic centimeters of the fat in 15 cubic centimeters of ether in a test tube. Stopper the tube with cotton wool loosely and allow to stand twelve to twenty-four hours at room temperature (20° to 25°). When crystals form at the bottom of the tube they are removed with a pipette or glass rod or tube, placed on a slide, covered, and examined. The crystals formed by later deposits may be examined in a similar way.

Sampling.—If large quantities of butter are to be sampled a butter trier or sampler may be used. The portions thus drawn, about 500 grams, are to be perfectly melted in a closed vessel at as low a heat as possible, and when melted the whole is to be shaken violently for some minutes till the mass is homogeneous. A portion is then poured into a vessel from which it is to be weighed out for analysis, and should nearly or quite fill it. This sample should be kept in a cold place till analyzed.

Determination of water.—1.5 to 2.5 grams are dried to constant weight at the temperature of boiling water in a dish with flat bottom, having a surface of at least 20 cm^2.

The use of clean, dry sand or asbestos with the butter is admissible, and is necessary if a dish with round bottom is employed.

Determination of fat.—The dry butter from the water determination is dissolved in the dish with *absolute* ether or with 76° benzine. The contents of the dish are then transferred to a weighed Gooch filter with the aid of a wash bottle filled with the solvent and are washed till free from fat. The crucible and contents are heated at the temperature of boiling water till the weight is constant. The weight of fat is calculated from the data obtained.

Substitute method for fat.—Water may be determined by drying the butter on asbestos or sand and the fat extracted by *anhydrous alcohol-free* ether in an extraction apparatus. The extract, after evaporation of the ether, is heated to constant weight at the temperature of boiling water and weighed.

Determination of casein and ash.—The crucible containing the residue from the fat determination, consisting of casein and ash, is covered and heated gently at first, gradually raising the temperature to just below red heat. The cover may then be removed and the heat continued till the contents of the crucible are white. The loss in weight of the crucible and contents represents casein, and the residue in the crucible, mineral matter. In this mineral matter, dissolved in water slightly acidulated, chlorine may be determined gravimetrically with silver nitrate, or volumetrically, using potassium chromate as indicator.

ESTIMATION OF SALT (NaCl).

Volumetric method.—The amount of the butter or butter substitute to be taken is from 5 to 10 grams; weigh in a counterpoised beaker-glass. The butter (fresh from the refrigerator) is placed in portions of about 1 gram at a time in the beaker, these portions being taken from different parts of the sample. By this means a reasonably fair sample of the whole is obtained.

The given quantity having been weighed out, it is removed from the pan.

Hot water is now added (about 20 cubic centimeters) to the beaker containing the butter, and after it has melted the liquid is poured into the bulb of the separating apparatus. The stopper is now inserted and the contents shaken for a few moments.

After standing until the fat has all collected on top of the water, the stop-cock is opened and the water, containing most of the salt, is allowed to run into an Erlenmeyer flask, being careful to let none of the fat globules pass.

Hot water is again added to the beaker and thence poured into the separatory apparatus, the bottle well shaken, and the foregoing process is repeated from ten to fifteen times, using each time 10 to 20 cubic centimeters of water.

The resulting washings contain all but a mere trace of the NaCl originally present in the butter.

Estimation of NaCl in filtrate.—The chloride of sodium is now determined in the filtrate by a standard solution of $AgNO_3$, using a few drops of a saturated solution of potassium chromate as indicator.

SPECIFIC GRAVITY.

Weight of flask.—Use a small specific gravity flask of from 25 to 30 cubic centimeters capacity. The stopper should be beveled to a fine edge on top and the lower end should be slightly concave to avoid any trapping of air. The flask is to be thoroughly washed with hot water, alcohol, and ether, and then dried for thirty minutes to one hour at 100°. After cooling in a desiccator the weight of the flask and stopper is accurately determined.

Weight of water.—The flask in an appropriate holder (Fig. 16), conveniently made of galvanized iron, is filled with freshly boiled and still hot distilled water and placed in a bath of pure, very hot, distilled water in such a way that it is entirely surrounded by the liquid with the exception of the top.

The water of the bath is kept in brisk ebullition for thirty minutes, any evaporation from the flask being replaced by the addition of boiling distilled water. The stopper* is then inserted, the flask removed, wiped dry, and after it is nearly cooled to room temperature, placed in the balance and weighed when balance temperature is reached. A convenient size of holder will enable the analyst to use eight flasks at once. The temperature at which water boils in each locality may also be determined; but unless at very high altitudes or on days of unusual barometric disturbance the variations will not be great, and will not appreciably affect the results.

* The stopper should be kept for a few minutes before use in hot distilled water.

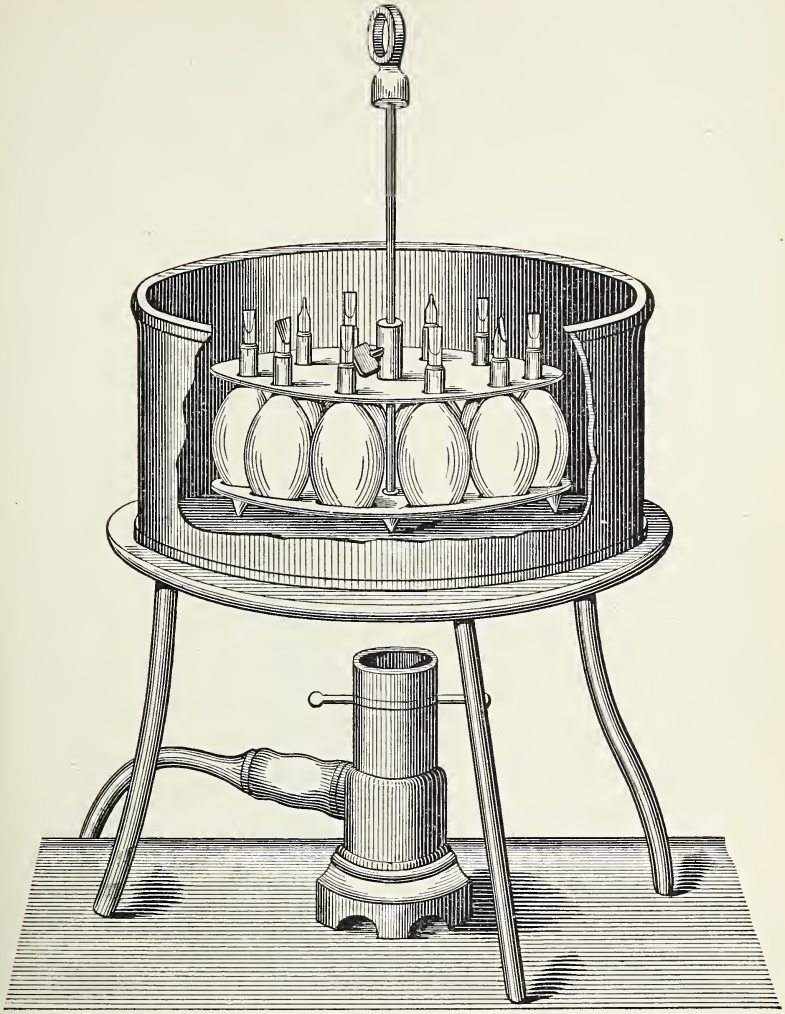

FIG. 16.

ALTERNATE METHOD OF ESTIMATING THE WEIGHT OF WATER IN FLASKS.

COMPUTATION BY THE FORMULA OF LANDOLT.

Formula for calculating volume V, in cubic centimeters, of a glass vessel from the weight P of water of temperature t contained therein, and the volume V′ at any other temperature t' (from Landolt and Börnstein's Physical-Chemical tables, p. 39, table 17):

$$V = P \frac{p}{d}$$

$$V' = P \frac{p}{d} \left[1 + \gamma (t' - t) \right]$$

p = weight (in brass weights) of 1 cubic centimeter H_2O in vacuo; see formula table 3. (This is so nearly 1 that it will not affect the result in the fifth place of decimals and may therefore be disregarded.) Hence the formula stands:

$$V' = P \frac{1}{d} \left[1 + \gamma (t' - t) \right]$$

d = density of water at temperature t (see table 12).

$\gamma = .000025$, the cubical expansion coefficient of glass.

From this volume the weight of the water may be readily obtained by referring to tables 13 and 13*a*.

Weight of fat at water-boiling temperature.—The flask is emptied of its water, rinsed with alcohol and ether, and dried again for a few minutes at 100°. It is then filled with the dry, hot, fresh-filtered fat, which should be entirely free from air bubbles.

The stoppered flask is then replaced in the water bath, kept for thirty minutes at the temperature of boiling water, removed and treated as above. The weight of fat having been determined, the specific gravity is obtained by dividing it by the weight of water previously found.

Example.

	Grams.
Weight of flask No. 22, dry	10.0197
Weight of flask No. 22, plus water	37.3412
Weight of water	27.3215
Weight of flask No. 22, plus fat	34.6111
Weight of fat	24.5914

Specific gravity=24.5914÷27.3215=.90008.

The weight of the flask dry and empty and the weight of water at 99° t› 100° contained therein may be used constantly if great care be taken in handling and cleaning the apparatus.

Example.

	Grams.
Weight of flask No. 10, dry and empty	10.0028
Weight of flask after three weeks' use	10.0030

MELTING POINT.

The apparatus for determining the melting point (shown in Fig. 17) consists of (1) an accurate thermometer for reading easily tenths of a degree; (2) a cathetometer for reading the thermometer (this may be done with an eyeglass, if held steadily and properly adjusted); (3) a thermometer; (4) a tall beaker glass, 35 centimeters high and 10 centimeters in diameter; (5) a test tube 30 centimeters long and 3.5 centimeters in diameter; (6) a stand for supporting the apparatus; (7) some method of stirring the water in the beaker, for example, a blowing bulb of rubber, and a bent glass tube extending to near the bottom of the beaker; (8) a mixture of alcohol and water of the same specific gravity as the fat to be examined.

MANIPULATION.

The disks of the fat are prepared as follows: The melted and filtered fat is allowed to fall from a dropping tube from a height of 15 to 20 centimeters onto a smooth piece of ice floating in water. The disks thus formed are from 1 to 1.5 centimeters in diameter and weigh about 200 milligrams. By pressing the ice under the water the disks are made to float on the surface, whence they are easily removed with a steel spatula, which should be cooled in the ice water before using.

The mixture of alcohol and water is prepared by boiling distilled water and 95 per cent alcohol for ten minutes to remove the gases which they may hold in solution. While still hot, the water is poured into the test tube already described until it is

nearly half full. The test tube is then nearly filled with the hot alcohol. It should be poured in gently down the side of the inclined tube to avoid too much mixing. If the tube is not filled until the water has cooled, the mixture will contain so many air bubbles as to be unfit for use. These bubbles will gather on the disk of fat as the temperature rises and finally force it to the top of the mixture.

The test tube containing the alcohol and water is placed in a tall beaker containing water and ice. The disk of fat is dropped into the tube from the spatula, and at once sinks until it reaches a part of the tube where the density of the alcohol-water is exactly equivalent to its own. Here it remains at rest and free from the action of any force save that inherent in its own molecules.

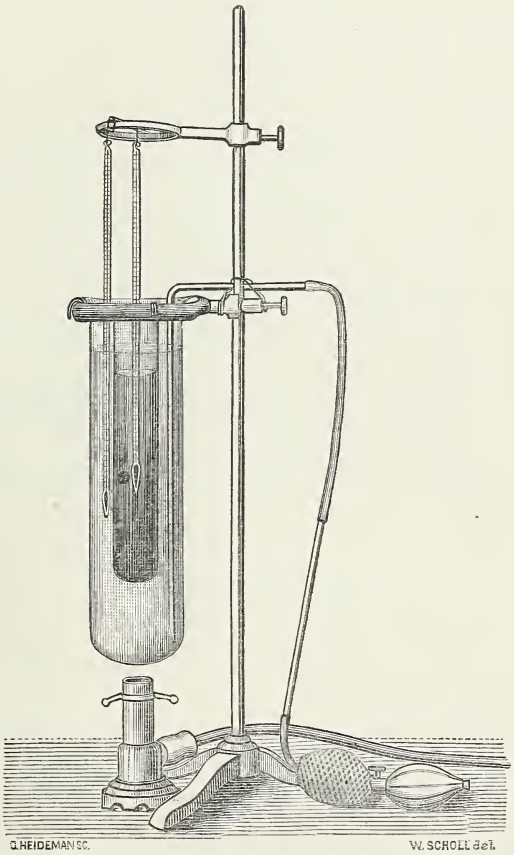

Fig. 17.

The delicate thermometer is placed in the test tube and lowered until the bulb is just above the disk. In order to secure an even temperature in all parts of the alcohol mixture in the vicinity of the disk the thermometer is moved from time to time in a circularly pendulous manner. A tube prepared in this way will be suitable for use for several days; in fact until the air bubbles begin to attach themselves to the disk of fat. In no case did the two liquids become so thoroughly mixed as to lose the property of holding the disk at a fixed point, even when they were kept for several weeks.

In practice, owing to the absorption of air, it has been found necessary to prepare new solutions every third or fourth day.

The disk having been placed in position, the water in the beaker glass is slowly heated and kept constantly stirred by means of the blowing apparatus already described.

When the temperature of the alcohol-water mixture rises to about 6° below the melting point the disk of fat begins to shrivel and gradually rolls up into an irregular mass.

The thermometer is now lowered until the fat particle is even with the center of the bulb. The bulb of the thermometer should be small, so as to indicate only the temperature of the mixture near the fat. A gentle rotary movement should be given to the thermometer bulb, which might be done with a kind of clock work. The rise of temperature should be so regulated that the last 2° of increment require about ten minutes. The mass of fat gradually approaches the form of a sphere, and when it is sensibly so the reading of the thermometer is to be made. As soon as the temperature is taken the test tube is removed from the bath and placed again in the cooler. A second tube, containing alcohol and water, is at once placed in the bath. The test tube (ice water being used as a cooler) is of low enough temperature to cool the bath sufficiently. After the first determination, which should be only a trial, the temperature of the bath should be so regulated as to reach a maximum about 1.5° above the melting point of the fat under examination.

Working thus with two tubes about three determinations can be made in an hour. After the test tube has been cooled the globule of fat is removed with a small cup attached to a wire before another disk of fat is put in.

The distilled water in which the piece of ice floats on which the disks are made should be recently boiled to free it of all air particles. It is important that the disks be free from air bubbles.

The edge of the disk should not be allowed to touch the sides of the tube. This accident rarely happens, but in case it should take place and the disk adhere to the sides of the tube a new trial should be made.

Triplicate determinations should be made and the second and third results should show a near agreement.

Example.

Melting point of sample of butter 6372 (No. 3):

	Degrees C.
(1)	33.15
(2)	33.05
(3)	33.00

ESTIMATION OF VOLATILE ACIDS.

Reagents.

SOLUTION OF CAUSTIC SODA.

1. 100 grams NaOH dissolved in 100 cubic centimeters pure water. The caustic soda should be as free as possible from carbonate and be preserved from contact with the air.

2. Alcohol, about 95 per cent redistilled with caustic soda.

3. Solution of sulphuric acid containing 25 cubic centimeters strongest H_2SO_4 in 1,000 cubic centimeters of water.

4. An accurately standardized approximately decinormal solution of barium hydrate.

5. Alcoholic solution of phenolphthalein.

APPARATUS.

1. Saponification flasks of hard, well-annealed glass, capable of resisting the tension of alcohol vapor at 100° C. The flask shown in Fig. 18 is most suitable for this purpose. It should have from 250 to 300 cubic centimeters capacity.

(*a.*) Instead of such a flask an Erlenmeyer flask of the same capacity fitted with long glass tube or reflux condenser may be used.

2. A pipette graduated to deliver 40 cubic centimeters.

3. Distilling apparatus as represented in Fig. 19. One with a smaller bulb tube may also be used.

4. An accurately calibrated burette reading to tenths of a cubic centimeter.

THE MANIPULATION.

Weighing the fat.—The butter or fat to be examined should be melted and kept in a dry warm place at about 60° C for two or three hours until the moisture and curd have entirely settled out. The clean supernatant fat is poured off and filtered through a dry filter paper in a jacketed filter containing boiling water, to remove all foreign matter and any traces of moisture. Should the filtered fat in a fused state not be perfectly clear the treatment above mentioned must be repeated.

The saponification flasks are prepared by having them thoroughly washed with water, alcohol, and ether, wiped perfectly dry on the outside and heated for one hour to 100° C (*circa*). The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within fifteen or twenty minutes of the time they are weighed. The weight of each flask is determined accurately, using a flask for a counterbalance or not, as may be convenient. The weight of the flasks having been accurately determined they are charged with the melted fat in the following way:

A pipette with a long stem marked to deliver 5.75 cubic centimeters is warmed to a temperature of about 50° C. The fat having been poured back and forth once or twice into a dry beaker in order to thoroughly mix it, it is taken up in the pipette, the nozzle of the pipette carried to near the bottom of the flask, it having been previously wiped to remove any adhering fat. The 5.75 cubic centimeters of fat are allowed to flow into the flask and the pipette is removed. After the flasks have been charged in this way they should be re-covered with the silk handkerchief and allowed to stand fifteen or twenty minutes, when they are again weighed.*

The saponification.—Ten cubic centimeters of 95 per cent alcohol redistilled from caustic soda are added to the fat in the flask, 2 cubic centimeters of the concentrated soda solution are added, a soft cork stopper inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flasks upon the water or steam bath as indicated in Fig. 18. The flasks during the saponification, which should last for one hour, should be gently rotated from time to time, being careful not to project the soap for any distance up the sides of the flask. At the end of an hour the flasks, after having been cooled to near the room temperature, are opened.

Removal of the alcohol.—The stoppers having been laid loosely in the mouth of the flasks the alcohol is removed by dipping the flasks into a steam bath. The steam

* Before weighing the flasks any desiccating material used in the balance should be removed. If round bottom flasks are employed, a special form of holder must be used. This is made on the principle of a test tube rack, the lower board of the tray being perforated so as to receive the round bottom of the flask and being protected by lugs, so that on being placed on a table the bottoms of the flasks do not touch the table.

Example:

	Grams.
Weight of counterbalanced flask No. 3	22.5904
Weight of counterbalanced flask No. 3 + fat	27.6734
Weight of fat	5.0830

should cover the whole of the flask except the neck. After the alcohol is nearly removed frothing may be noticed in the soap, and to avoid any loss from this cause or any creeping of the soap up the sides of the flask it should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapor may be removed from the flask by waving it briskly, mouth down, to and fro. Complete removal of the alcohol with the precautions above noted should take about forty-five minutes.

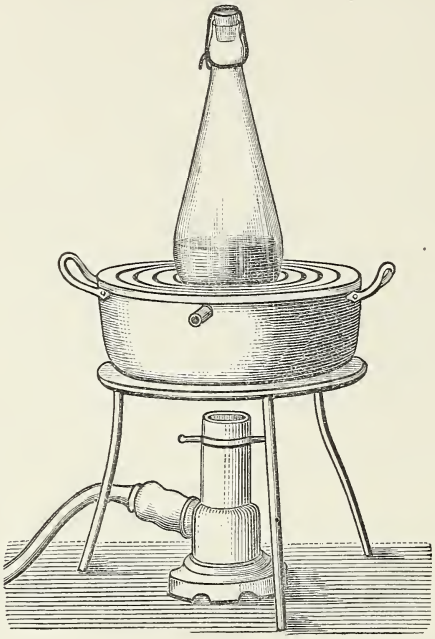

Fig. 18.

Dissolving the soap.—After the removal of the alcohol the soap should be dissolved by adding 100 cubic centimeters of recently boiled distilled water, and warmed on the steam bath with occasional shaking until the soap is completely dissolved.

Setting free the fatty acids.—When the soap solution has cooled to about 60° or 70° C the fatty acids are separated by adding 40 cubic centimeters of the dilute sulphuric acid solution mentioned above.

Melting the fatty acid emulsion.—The flasks should now be restoppered as in the first instance, and the fatty acid emulsion melted by replacing the flasks on the steam bath. According to the nature of the fat examined the time required for the fusion of the fatty acid emulsions may vary from a few minutes to hours.

The distillation.—After the fatty acids are completely melted, which can be determined by their forming a transparent oily layer on the surface of the water, the flasks are cooled to room temperature and a few pieces of pumice stone added. The pumice stone is prepared by throwing it, at white heat, into distilled water and keeping it under water until used. The flask is now connected with a condenser (Fig. 19) slowly heated with a naked flame until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 110 cubic centimeters of the distillate in as nearly as possible thirty minutes. The distillate should be received in flasks accurately graduated at 110 cubic centimeters.

Titration of the volatile acid.—The 110 cubic centimeters of distillate, after thorough mixing, are filtered through perfectly dry filter paper and collected in a flask graduated

at 100 cubic centimeters. The 100 cubic centimeters of the filtered distillate are poured into a beaker holding from 200 to 250 cubic centimeters, 0.5 centimeters phenolphthalein solution added, and decinormal barium hydrate run in until a red color is produced. The contents of the beaker are then returned to the measuring flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red color produced remains apparently unchanged for two or three minutes.

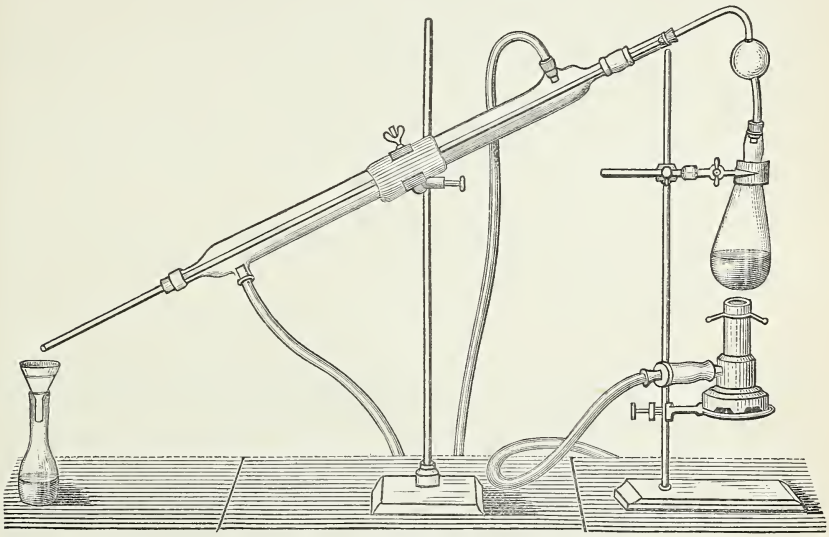

FIG. 19.

ALTERNATE METHOD OF DETERMINING VOLATILE ACIDS.

SAPONIFICATION WITHOUT THE USE OF ALCOHOL.

To avoid the danger of loss from the formation of ethers and the trouble of removing the alcohol after saponification the fat may be saponified with a solution of caustic potash in a closed flask without alcohol. The operation is carried on exactly as indicated above for saponification in a closed flask, using caustic potash solution instead of soda, and omitting the operation for volatilizing the alcohol. The caustic potash is prepared as follows: Dissolve 100 grams of the purest potassium hydrate in 58 grams of hot distilled water. Allow to cool in a stoppered vessel, decant the clear caustic solution, and preserve in a vessel out of contact with the air. For the saponification use 2 cubic centimeters of the caustic potash solution, which is poured on the fat after it has solidified in the flask. Great care must be taken that none of the fat is allowed to rise on the sides of the saponifying flask to a point where it can not be reached by the alkali. During the process of saponification the flask can only be very gently rotated in order to avoid the difficulty mentioned above. This process is not recommended in any except a closed flask with round bottom. In the subsequent solution of the soap use only 80 cubic centimeters of distilled water and in setting free the fatty acids use 60 cubic centimeters of the dilute sulphuric acid. In other respects the distillation is conducted as described. Potash is used instead of soda, so as to form a softer soap and thus allow a more perfect saponification.

The saponification may also be conducted as follows: The alkali and fat in the melted state are shaken vigorously in the saponification flask until a complete emulsion is secured. The rest of the operation is then conducted as above.

Iodine Equivalent.

REAGENTS.

1. Dissolve 25 grams of pure iodine in 500 cubic centimeters of 95 per cent alcohol. Dissolve 30 grams of mercuric chloride in 500 cubic centimeters of 95 per cent alcohol. The last solution, if necessary, is filtered and then the two solutions mixed. The mixed solution should be allowed to stand twelve hours before using.

2. *Decinormal hyposulphite of sodium solution.*—Take 24.6 grams of chemically pure hyposulphite of soda freshly pulverized as finely as possible and dried between filter or blotting paper. Make this up to 1,000 cubic centimeters at the temperature at which the titrations are to be made.

3. *Starch paste.*—One gram of starch boiled in 200 cubic centimeters of distilled water for ten minutes and cooled to room temperature.

4. *Solution of iodide of potassium.*—150 grams of iodide of potassium dissolved in water and made up to 1 liter.

5. *Solution of bichromate of potassium.*—Dissolve 3.874 grams chemically pure bichromate of potassium in distilled water and make the volume up to 1 liter at the temperature at which the titrations are to be made.

MANIPULATION.

Standardizing the hyposulphite of sodium solution.—Run 20 cubic centimeters of the bichromate of potassium solution into a glass stoppered flask to which has been added 10 cubic centimeters of the solution of iodide of potassium. Add to this 5 cubic centimeters of strong hydrochloric acid. Allow the solution of hyposulphite of sodium to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste and with constant shaking continue to add the hyposulphite of sodium solution until the blue color just disappears. The number of cubic centimeters of hyposulphite solution used multiplied by 5 is equivalent to 1 gram of iodine.

Example.—20 cubic centimeters $K_2Cr_2O_7$ solution required 16.2 cubic centimeters hyposulphite of soda; then $16.2 \times 5 = 81 =$ number cubic centimeters of hyposulphite solution equivalent to 1 gram of iodine. Then 1 cubic centimeter hyposulphite solution = 0.0124 gram of iodine. Theory for decinormal solution of hyposulphite of sodium, 1 cubic centimeter = 0.0127 gram of iodine.

Weighing the sample.—About 1 gram of butter fat is to be weighed in a glass-stoppered flask holding about 300 cubic centimeters with the precautions mentioned for weighing the fat for determining volatile acids.

Absorption of iodine.—The fat in the flask is dissolved in 10 cubic centimeters of chloroform. After complete solution has taken place 30 cubic centimeters of the iodine-mercuric chloride solution are added. The flask is now placed in a dark place and allowed to stand with occasional shaking for three hours.

Titration of the unabsorbed iodine.—100 cubic centimeters of distilled water are added to the contents of the flask, together with 20 cubic centimeters of the iodide of potassium solution. Any iodine which may be noticed upon the stopper of the flask should be washed back into the flask with the iodide of potassium solution. The excess of iodine is now oxidized with the hyposulphite of sodium solution, which is run in gradually with constant shaking until the yellow color of the solution has almost disappeared. A few drops of starch paste are then added and the titration continued until the blue color has entirely disappeared. Toward the end of the reaction the flask should be stoppered and violently shaken so that any iodine remaining in solution in the chloroform may be taken up by the iodide of potassium solution in the water. A sufficient quantity of hyposulphite of sodium solution should be added to prevent a reappearance of any blue color in the flask for five minutes.

Setting the value of the iodine solution by the hyposulphite solution.—At the time of

adding the iodine solution to the fats two blank flasks of the same size and nature as those used for the determination should be employed for conducting the operation described above without the presence of any fat. In every other respect the conduct of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used.

EXAMPLE.

BLANK DETERMINATIONS.

(1) 30 cubic centimeters iodine solution requires 46.4 cubic centimeters hyposulphite of sodium solution.

(2) 30 cubic centimeters iodine solution requires 46.8 cubic centimeters of hyposulphite of sodium solution.

Mean 46.6.

PERCENTAGE OF IODINE ABSORBED.

Weight of fat taken	grams..	1.0479
Quantity of iodine solution used	cubic centimeters..	30
Hyposulphite equivalent of iodine used	do	46.6
Hyposulphite to oxidize remaining iodine	do	14.7
Hyposulphite equivalent to iodine absorbed	do	31.9

Percentage of iodine absorbed, $31.9 \times 0.0124 \times 100 \div 1.0479 = 37.75$ per cent.

ELECTIVE DETERMINATIONS.

For the further study of the properties of butter the following recommendations are made, to be followed by the analyst or not as he may elect:

Reduction of silver.—To determine whether or not the butter has been derived from a cow fed on cotton-seed meal it will usually be sufficient to test the sample by Bechi's reagent.

The solutions used are as follows: Five grams of silver nitrate dissolved in 100 cubic centimeters, 95 per cent alcohol, and 1 cubic centimeter of strong nitric acid added. The manipulation is conducted as follows: Measure out 5 cubic centimeters of the fat into a small porcelain dish and add 5 cubic centimeters of the above reagent. Stir together thoroughly with a stirring rod and place upon the steam bath for ten minutes. Notice the changes of color which take place, the intensity of the color produced, and the amount of silver deposited as a mirror on the sides of the dish.

Reduction test applied to the fatty acids.—Instead of testing the original glycerides as above the test may be applied to the fatty acids in accordance with the following directions:

Reagent.—Dissolve 30 grams of nitrate of silver in 100 cubic centimeters of water.

Manipulation.—Place 5 cubic centimeters of the fatty acid in the porcelain dish which is used above and dissolve in 20 cubic centimeters of 95 per cent alcohol. Add 2 cubic centimeters of the reagent, stir thoroughly together, and heat on the water bath as in the first instance.

Melting point of the fatty acids.—The melting point of the fatty acids may be determined as described in Part 4, Bulletin No. 13, page 448.

The melting point of the fatty acids can not be determined in the same apparatus and by the same methods as those described for the fats themselves, because the acids are soluble in alcohol. It should be remembered that the melting point of the fatty acids is slightly above that of the glycerides, and the first determination in every case should be solely for the purpose of determining approximately the temperature at which the fat melts.

The bulb of a delicate thermometer is coated with the fatty acid, and the thermom-

eter by means of a cork is fastened in a round flask of 250 cubic centimeters capacity. The bulb of the instrument should occupy as nearly as possible the center of the flask. The cork should have an air passage for the equalization of the pressure. The flask is slowly heated in a current of warm air, or otherwise, and as the melting point is approached a rotary motion is given to it. When the fat melts it is seen to collect in a small drop on the lowest part of the bulb, remaining stationary while the flask is turned. The thermometer is best held horizontally.

Crystallizing point of the fatty acids.—The crystallizing point of the fatty acid is determined by means of the method described in Bulletin No. 13, Part 4, page 447.

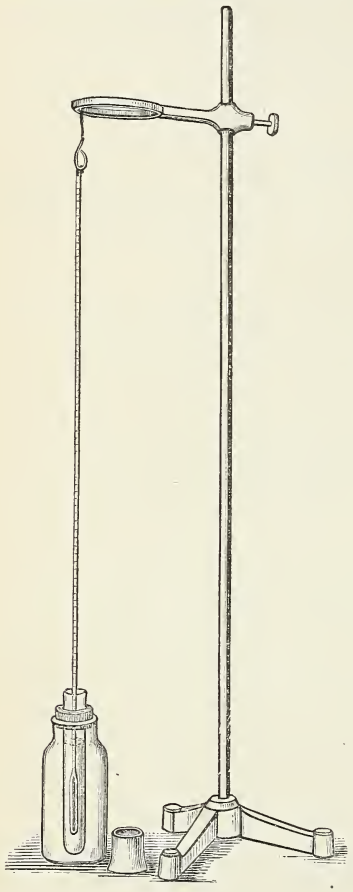

FIG. 20.

A very delicate thermometer with a long bulb is used, the thermometer being graduated to tenths of a degree; the readings of the mercury are made with a small eyeglass. A test tube about 15 centimeters in length and 2.5 to 3 centimeters in diameter is filled with the melted fatty acids. The temperature at which the acid is melted should be sufficiently high to secure a complete liquefaction. The tube containing the fat is placed in a stopper carried in a bottle so that the whole of the fatty acid may be contained in that part of the tube protected from external currents of air by the bottle. The bottom of this protected bottle should be warm so that its temperature may be several degrees higher than the crystallizing point of the fatty acid. This precaution is necessary to avoid a too rapid crystallization of the fatty acid in the bottom of the test tube, and to secure as nearly as possible a uniform crystallization throughout the whole mass. The thermometer is suspended in such a manner that the bulb may occupy as nearly as possible the center of the fatty mass. The thermometer should be protected from currents of air and should be kept perfectly still. The position of the mercury in the thermometer is carefully watched by the attendant as it gradually sinks toward the crystallizing point. When the crystals of the acid begin to appear in the bottom and on the sides of the test tube the descent of the mercury will become very slow and finally cease. The lowest point reached by the mercury should be noted. As the crystallization extends inward toward the bulb of the thermometer a point will be reached when the mercury will begin to rise. At that point, the test tube being held by the left hand, the thermometer should be taken by the right hand of the operator, and the partially crystallized mass of fat thoroughly stirred by turning the thermometer three or four times around the tube in both directions. Care should be exercised that at the end of this operation the bulb of the thermometer should hang as near as possible in the center of the crystallizing mass. Directly the above operation is accomplished the mercury will be seen to rise, and this rise of temperature will continue for some time, after which the mercury will remain stationary for one or two minutes. The highest point reached is taken as the true temperature of crystallization.

Refractive index.—The refractive index is conveniently determined by the apparatus of Professor Abbe, Fig. 21. The manipulation is conducted as follows: Fine tissue

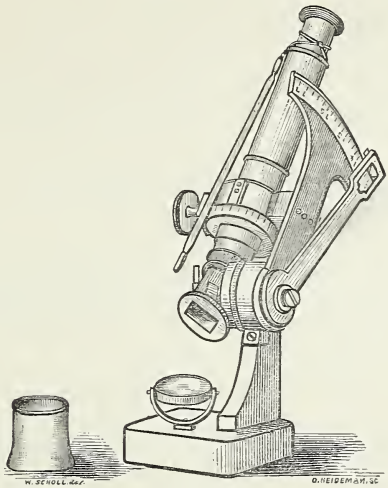

FIG. 21.

paper or rather heavy body is cut into rectangular pieces 3 centimeters in length by 1.5 centimeters in breath. One of these pieces of paper is placed on the lower of the two glass prisms of the apparatus. Two or three drops of the oil or fat are placed upon the paper and the upper prism carefully placed in position so as not to move the paper from its place. In charging the apparatus with the oil in this way, it is placed in the horizontal position. After the paper disk holding the fat is secured by replacing the upper prism, the apparatus is placed in its normal position and the index moved until the light directed through the apparatus by the mirror shows the field of vision divided into dark and light portions. The dispersion apparatus is now turned until the rainbow colors on the part between the dark and light field have disappeared. Before doing this, however, the telescope, the eyepiece of the apparatus, is so adjusted as to bring the cross lines of the field of vision distinctly into focus. The index of the apparatus is now moved back and forth until the dark edge of the field of vision falls exactly in the intersection of the cross lines. The refractive index of the fat under examination is then read directly upon the scale by means of a small magnifying glass. To check the accuracy of the first reading, the dispersion apparatus should be turned through an angle of 180° until the colors have again disappeared and the scale of the instrument again read. Those two readings should fall closely together, and their mean is the true reading of the fat under examination.

For butter fats the apparatus should be kept in a warm place, the temperature of which does not fall below 30° C. For reducing the results obtained to a standard temperature, say 25° C, the following factor may be used. The mean rate of variation in the refractive index of butter fats for each degree of temperature was determined by me in twelve samples of butter fat (see Journal of Analytical Chemistry, Vol. 2, Part 3, July, 1888). This factor is .000176. As the temperature rises the refractive index falls.

Example.

Refractive index of a butter fat determined at 32° 4=1.4540, reduced to 25° C, as follows: $32.4 - 25 = 7.4 = 0.0013$; then $1.4540 + 0.0013 = 1.4553$.

The instrument used should be set with distilled water at 25° C, the theoretical refractive index of water at that temperature being 1.3330. In the determination above

given the refractive index of pure water measured 1.3300; hence the above numbers should be corrected for theory by the addition of 0.0030, making the corrected index of the butter fat mentioned at the temperature given, 1.4583.

Soluble and insoluble acids.—Use method described in Bulletin 13, Part 4, pages 455 to 461.

Saponification equivalent.—Use method described in Bulletin 13, Part 4, pages 461, 462.

Rise of temperature with sulphuric acid.—Use method described in Bulletin 13, Part 4, pages 443–446.

METHODS FOR MILK ANALYSIS.

WATER.

Evaporate 1 to 2 grams of milk in a tared flat dish containing from 15 to 20 grams of pure dry sand, or without sand, until apparently dry. Transfer to air bath and dry for one hour at temperature of boiling water. Cool in desiccator and weigh rapidly to avoid absorption of hygroscopic moisture.

TOTAL NITROGENOUS MATTER.

Place in a Kjeldahl digestion flask a known weight (about 5 grams) of milk and proceed exactly as described for this method by the nitrogen reporter.

FAT; METHOD OF ADAMS, MODIFIED BY WILEY.

Coils made of thick filter paper, cut into strips 2.5 by 25 inches, are thoroughly extracted with ether and alcohol or the weight of the extract corrected by a constant obtained for the paper. About 5 cubic centimeters of the well mixed milk are placed in a small beaker, covered with a watch glass, and weighed. From a weighing bottle about 5 grams of milk are transferred to the coil by a pipette, care being taken to keep the end of the coil held in the fingers dry. The coil, dry end down, on a piece of glass is dried at the temperature of boiling water for one hour, or better dried in hydrogen at temperature of boiling water, transferred to a syphon extraction apparatus and extracted by at least 12 syphonings with absolute ether or petroleum spirit boiling at about 45° C. The extracted fat is dried in hydrogen and weighed.

ALTERNATE METHOD OF ESTIMATING WATER AND FAT IN MILK.

Method of Babcock.—In the bottom of a perforated test-tube is placed a clump of clean cotton, the tube is then filled three-quarters full of ignited asbestos, lightly packed, and a plug of cotton inserted over it. The tube and contents are weighed and the plug of cotton carefully removed and 5 grams of milk from a weighed pipette run into it, and the plug of cotton replaced. The tube connected at its lower end by a rubber tube and adapter with a filter pump is placed in a drying oven at a temperature of 100° C., and a slow current of dry air drawn through it until the water is completely expelled, which in no case requires more than two hours.

The tube containing the solids from the above operation is placed in an extraction apparatus and exhausted with ether in the usual way.

THE ESTIMATION OF SUGAR.

The reagents, apparatus, and manipulation necessary to give the most reliable results in milk-sugar estimation are as follows:

Reagents.—(1) *Basic plumbic acetate*, specific gravity 1 97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One cubic centimeter of this will precipitate the albumens in 50 to 60 cubic centimeters of milk.

(2) *Acid mercuric nitrate.* Dissolve mercury in double its weight of nitric acid, specific gravity 1.42. Add to the solution an equal volume of water. One cubic centimeter of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarization.

(3) *Mercuric iodide with acetic acid.* KI 33.2 grams, $HgCl_2$ 13.5 grams, $C_2H_4O_2$ 20 cubic centimeters, H_2O 64 cubic centimeters.

Apparatus.—(1) Pipettes marked at 59.5, 60, and 60.5 cubic centimeters. (2) Sugar flasks marked at 102.4 cubic centimeters. (3) Filters, observation tubes, and polariscope. (4) Specific gravity spindle and cylinder. (5) Thermometers.

Manipulation.—(1) The room and milk should be kept at a constant temperature. It is not important that the temperature should be of any given degree. The work can be carried on equally well at 15° C., 20° C., or 25° C. The slight variations in rotary power within the above limits will not affect the result for analytical purposes. The temperature selected should be the one which is most easily kept constant.

(2) The specific gravity of the milk is determined. For general work this is done by a delicate specific gravity spindle. Where greater accuracy is required use specific gravity flask.

(3) If the specific gravity be 1.026, or nearly so, measure out 60.5 cubic centimeters into the sugar flask. Add one cubic centimeter of mercuric nitrate solution, or 30 cubic centimeters mercuric iodide solution, and fill to 102.4 cubic centimeter mark. The precipitated albumen occupies a volume of about 2.44 cubic centimeters. Hence the milk solution is really 100 cubic centimeters. If the specific gravity is 1.030, use 60 cubic centimeters of milk. If specific gravity is 1.034, use 59.5 cubic centimeters of milk.

(4) Fill up to mark in 102.4 cubic centimeter flask, shake well, filter, and polarize.

NOTES.—In the above method of analysis the specific rotatory power of milk sugar is taken at 52.5, and the weight of it in 100 cubic centimeter solution to read 100 degrees in the cane-sugar scale at 20.56 grams. This is for instruments requiring 16.19 grams, sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk-sugar, whatever instrument is employed.

Since the quantity of milk taken is three times 20.56 grams, the polariscopic readings divided by 3 give at once the percentage of milk sugar when a 200-millimeter tube is used.

If a 400-millimeter tube is employed, divide reading by 6; if a 500-millimeter tube is used, divide by 7.5.

Since it requires but little more time, it is advisable to make the analysis in duplicate and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102.4 for 60 cubic centimeters no correction for volume of precipitated casein need be made. In no case is it necessary to heat the sample before polarizing.

ALTERNATE METHOD.

The sugar may also be determined either gravimetrically or volumetrically by alkaline copper solution.

ESTIMATION OF ASH.

Evaporate to dryness in a weighed platinum dish 20 cubic centimeters of milk from a weighing bottle, to which 6 cubic centimeters of HNO_3 has been added, and burn at low red heat until ash is free from carbon.

METHODS OF DETERMINING POTASH.

METHOD OF LINDO AS MODIFIED BY GLADDING.

(1) *Superphosphates.*—Pulverize the fertilizer (200 or 300 grams) in a mortar. Boil 10 grams with 300 cubic centimeters of water for thirty minutes; add ammonia in

slight excess and then a little oxalate of ammonia, thus precipitating all phosphate and sulphate of lime, oxide of iron, and alumina, etc.; make up to 500 cubic centimeters, mix thoroughly, and filter through a dry filter; take 50 cubic centimeters, corresponding to 1 gram, evaporate nearly to dryness, add 1 cubic centimeter of dilute H_2SO_4 (1 to 1), and evaporate to dryness and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by volatilization of potash, and a full red heat must be used until the residue is perfectly white. This residue is dissolved in hot water plus a few drops of HCl, 5 cubic centimeters of a solution of pure NaCl (containing 20 grams NaCl to the liter), and an excess of platinum solution (4 cubic centimeters) are now added. This solution is then evaporated to dryness in a small dish, the residue taken up with a little water sufficient to dissolve it, and strong alcohol added. The precipitate is washed thoroughly with alcohol by decantation and on filter as usual. The washing should be continued even after the filtrate is colorless. Ten cubic centimeters of the NH_4Cl solution prepared as directed are now run through the filter, or the washing may be performed in the dish. This 10 cubic centimeters will contain the bulk of the impurities, and is thrown away. Fresh portions of 10 cubic centimers NH_4Cl are now run through the filter several times (five or six). The filter is then washed thoroughly with pure alcohol, dried, and weighed as usual. The platinum solution used contains 1 gram metallic platinum in every 10 cubic centimeters.

(2) *Muriates of potash.*—In the analysis of these salts an aliquot portion, containing 0.500 gram, is evaporated with 10 cubic centimeters platinum solution plus a few drops of HCl, and washed as before.

(3) *Sulphate of potash, kainite, etc.*—In the analysis of these salts an aliquot portion containing 0.500 gram is taken, 0.250 gram of NaCl added, plus a few drops of HCl, and the whole evaporated with 15 cubic centimeters platinum solution. In this case special care must be taken in the washing with alcohol to remove all the double chloride of platinum and sodium. The washing should be continued for some time after the filtrate is colorless. Twenty-five cubic centimeters of the NH_4Cl solution are employed instead of 10 cubic centimeters, and the 25 cubic centimeters poured through at least six times to remove all sulphates and chlorides. Wash finally with alcohol, dry, and weigh as usual.

(4) *Organic compounds.*—In case the potash is contained in organic compounds like tobacco stems, cotton-seed hulls, etc., weigh out 10 grams, saturate with strong sulphuric acid, and ignite in a muffle to destroy organic matter; then proceed as under (1). To prepare the washing solution of NH_4Cl, place in a bottle 500 cubic centimeters H_2O, 100 grams of NH_4Cl; shake till dissolved. Now pulverize 5 or 10 grams of K_2PtCl_6, put in a bottle, and shake at intervals for six or eight hours; let settle overnight; then filter off liquid into a second bottle. The first bottle is then ready for a preparation of a fresh supply when needed.

ALTERNATE METHODS.

Prepare the fertilizer as for the Lindo-Gladding method; take 10 grams, boil for ten minutes with 200 cubic centimeters water, and after cooling, and without filtering, make up to 1,000 cubic centimeters, and filter through a dry paper. If the sample have 10 to 15 per cent K_2O (kainite), take 50 cubic centimeters of the filtrate; if from 2 to 3 per cent K_2O (ordinary potash fertilizers), take 100 cubic centimeters of the filtrate, In each case make the volume up to 150 cubic centimeters, heat to 100° C, and add, drop by drop, with constant stirring, slight excess of barium chloride; without filtering, in the same manner, add barium hydrate in slight excess. Heat, filter, and wash until precipitate is free of chlorides. Add to filtrate 1 cubic centimeter strong ammonium hydrate and then a saturated solution of ammonium carbonate, until excess of barium is precipitated. Heat. Add now, in fine powder, 0.5 gram pure oxalic acid or 0.75 gram ammonium oxalate. Filter, wash free of chlorides; evaporate filtrate to dryness in a platinum dish, and holding dish with crucible tongs, ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 cubic centimeters or more. To this filtrate, after adding two drops of strong hydrochloric acid, is added, in a porcelain dish, 5 to 10 cubic centimeters of a solution of 10 grams of platinic chloride in 100 cubic centimeters of water. The mixture is now evaporated on the water bath to a thick sirup, or further, as above treated with strong alcohol, washed by decantation, collected in a Gooch crucible or other form of filter, washed with strong alcohol, afterwards with 5 cubic centimeters ether, dried for thirty minutes at 100° C., and weighed.

It is desirable, if there is an appearance of foreign matter in the double salt, that it should be washed, according to the previous method, with 10 cubic centimeters of the half-concentrated solution of NH_4Cl, which has been saturated by shaking with K_2PtCl_6, as recommended by Gladding.

The use of the factor 0.3056 for converting K_2PtCl_6 to KCl and 0.19308 for converting to K_2O are continued.

THE OFFICIAL METHOD FOR THE ANALYSIS OF NON-STARCHY FOODS (COARSE FODDERS, OIL SEEDS, AND OTHER RESIDUES) FOR 1890–'91.

PREPARATION OF THE SAMPLE.

The substance is to be ground till all of it will pass through a sieve with circular holes 1 millimeter in diameter.

HYGROSCOPIC WATER.

Dry 2 to 3 grams of the substance for four hours, heated fully to the temperature of boiling water, in a current of dry hydrogen, but without allowing the glass containing it to come in contact with the boiling water.

ASH.

Char the substance at a low red heat, which is conveniently done in a Fletcher gas muffle furnace, heated not by the large gas burner that is supplied with the furnace, but by a Fletcher solid flame burner (No. 46b.); exhaust this charred mass with water; collect the insoluble residue on a filter, burn, add this ash to the residue from the evaporation of the above aqueous extract and heat the whole to low redness till the ash is white.

ETHER EXTRACT.

Extract 2 to 3 grams of the substance dried as for the determination of the moisture, with anhydrous and alcohol-free ether, sixteen hours. Dry the extract by exposure to the full heat of boiling water, in a current of dry hydrogen, to constant weight.

CRUDE PROTEIN.

Determine nitrogen by the Kjeldahl method as directed for nitrogen in fertilizers, and multiply the result by 6.25 for the crude protein.

ALBUMINOID NITROGEN.

Stutzer's method.—Prepare cupric hydrate as follows: Dissolve 100 grams of pure cupric sulphate in 5 liters of water, and add 2.5 cubic centimeters of glycerine; add dilute solution of sodium hydrate until the liquid is alkaline; filter; rub the precipitate up with water containing 5 cubic centimeters of glycerine per liter, and then wash by decantation or filtration until the washings are no longer alkaline. Rub

the precipitate up again in a mortar with water containing 10 per cent of glycerine, thus preparing a uniform gelatinous mass that can be measured out with a pipette. Determine the quantity of cupric hydrate per cubic centimeter of this mixture. To 1 gram of this substance add 100 cubic centimeters of water in a beaker, heat to boiling, or in the case of substances rich in starch heat on the water bath ten minutes, add a quantity of cupric hydrate mixture containing 0.7 to 0.8 grams of the hydrate, stir thoroughly, filter when cold, wash with cold water, and put the filter and its contents into the concentrated sulphuric acid for the determination of nitrogen after Kjeldahl. For the above filtration use Schleicher and Schüll's No. 589 paper, or Swedish paper, either of which contains so little nitrogen that it can be left out of account.

If the substance examined consists of seed of any kind, or residues of seeds, such as oil cake or anything else rich in alkaline phosphate, add a few cubic centimeters of a concentrated solution of alum just before adding the cupric hydrate, and mix well by stirring. This serves to decompose the alkaline phosphate. If this is not done cupric phosphate and free alkali may be formed and the protein copper may be partially dissolved in the alkaline liquid.

CRUDE FIBER.

Extract 2 grams of the substance with ordinary ether, at least nearly completely; or take the residue from the determination of the ether extract. To this residue, in a 500 cubic centimeter (Erlenmeyer) flask, add 200 cubic centimeters of boiling 1.25 per cent sulphuric acid; connect the flask with a return-flow condenser, the tube of which passes only a short distance beyond the rubber stopper into the flask. Boil at once, and continue the boiling for thirty minutes. A blast of air conducted into the flask may serve to reduce the frothing of the liquid.

Filter; wash thoroughly with boiling water till the washings are no longer acid; rinse the substance back into the same flask with 200 cubic centimeters of a boiling 1.25 per cent solution of sodium hydrate at least almost free from sodium carbonate; boil at once, and continue the boiling for thirty minutes in the same manner as directed above for the treatment with acid. Filter in a Gooch crucible and wash with boiling water till the washings are neutral; dry at 110° C.; weigh; incinerate completely, and give the loss of weight for crude fiber.

The filter used for the first filtration may be linen, one of the forms of glass wool, and asbestos filters recommended in the last report, or any other form that secures clear and reasonably rapid filtration. The carbonate free sodium hydrate can be obtained of the Troy Laundry Machinery Company, 32 Dey street, New York, or 297 Wabash avenue, Chicago, under the name of "Greenbank Alkali Company," double refined 98 per cent caustic soda, it being the same as that recommended for the Kjeldahl nitrogen method. The solutions of sulphuric acid and sodium hydrate are to be made up of the specified strength accurately by titration, and not merely by the areometer.

METHODS OF SUGAR ANALYSIS.

By the term "sugar analysis" it is understood that the analyses of all the common saccharine substances, viz, sugar, molasses, sirup, starch, sugar, and honey are embraced. In the following directions an attempt will be made to indicate the general principles which should guide the practice of sugar analysis, together with sufficient detail to enable these analyses to be carried out with accuracy and uniformity.

The principal components to be determined in the substances mentioned above are;

1. Water.
2. Ash.
3. Nitrogenous bodies,
4. Reducing sugar,
5. Sucrose.
6. Lactose.
7. Starch sugar,
8. Raffinose,

WATER.

In sugar or melada.—Weigh from 2 to 5 grams into a flat dish (nickel or platinum) and dry at temperature of boiling water for three hours; cool in desiccator and weigh; return to oven and dry for one hour. If on weighing there is only a slight change of weight, the process may be considered finished; otherwise the drying must be continued until the loss of water in one hour is not greater than 0.20 per cent.

In honey or molasses.—(*a*) Proceed as above, using only 1 to 2 grams of substance.

(*b*) Place 2 to 3 grams of substance in a flat dish holding from 30 to 50 cubic centimeters; dissolve in 70 per cent alcohol, using a small stirring rod, which is weighed with the dish. Add from weighing bottle 15 to 25 grams pure dry sand; dry in oven at 70° to 80° C. until alcohol is nearly driven off; moisten thoroughly with 99 per cent to absolute alcohol; dry at 75° C. for thirty minutes, then at temperature of boiling water for an hour; repeat as above, deduct weight of added sand, and make usual calculations.

ASH.

(*a*) Take 5 to 10 grams of the material (sugar, molasses, honey) in platinum dish* of 50 to 100 cubic centimeters capacity; heat at 100° C. until water is expelled and then slowly until intumescence ceases. The dish is then placed in muffle and heated at low redness until a white ash is obtained.

(*b*) *Soluble ash.*—Digest ash with water, filter onto Gooch crucible, wash with hot water, dry residue at 100° C., and weigh. Difference of weights equals soluble ash.

(*c*) Use 50 mg. zinc oxide to 25 grams molasses or 50 grams sugar. Incorporate thoroughly by adding dilute alcohol and mixing; dry and ignite as above. Deduct weight of zinc used from weight of ash.

(*d*) Carbonize the mass at a low heat; dissolve soluble salts with hot water; burn residual mass as above, add the solution of soluble salts, and evaporate to dryness at 100° C.; ignite gently, cool in desiccator, and weigh.

(*e*) Saturate sample with H_2SO_4, dry, ignite gently, then burn in muffle at low redness.

(*f*) Dissolve 10 grams of sugar in hot water and filter to remove sand, etc.; evaporate filtrate and washings to dryness; carefully carbonize and extract with hot water until there is no longer any reaction for chlorine. Dry and ignite residue; weigh as insoluble ash. Add the soluble portion, treat with HCl in slight excess, and evaporate to dryness. Heat until all free HCl is driven off; take up with H_2O and a little HCl, filter and wash. The residue is silica. Add NH_4OH to filtrate, boil and filter, wash residue, which is iron and alumina. To filtrate add $(NH_4)_2C_2O_4$, evaporate to dryness; ignite and moisten with $(NH_4)_2CO_3$ and reignite; dissolve in water, filter, and wash. Residue equals carbonates of Ca and Mg. Evaporate filtrate to small bulk, add $(NH_4)_2CO_3$, and evaporate to dryness; drive off excess of ammonia cautiously and weigh. This gives the alkalies as carbonates, and this weight added to the insoluble ash, formerly determined, gives the total carbonate ash.

NITROGENOUS BODIES.

Any of the methods adopted by the association for the estimation of nitrogen may be used.

REDUCING SUGAR.

Reagent, alkaline copper solution. (*Fehling, Violette*)

34.64 grams pure crystallized copper sulphate.
187.00 grams tartrate soda and potash.
78.00 grams caustic soda.

* If the substance contains tin or other metal capable of uniting with platinum a dish made of some other material must be used.

Dissolve the $CuSO_4 + 5H_2O$ and make up to 1,000 cubic centimeters at the average temperature at which the analyses are made. Mix the solutions of Rochelle salts and caustic soda and make up to 1,000 cubic centimeters. In practice use equal volumes of each reagent.

Processes (*volumetric*).—(*a*) The solution to be examined should contain about 1 per cent of reducing sugar. To 10 cubic centimeters of the copper solution and 10 cubic centimeters of the alkali, in a large test tube, add 20 cubic centimeters of water and boil. Add the sugar solution in approximately the proper quantity to reduce the copper, and boil for exactly two minutes. If, on standing for a moment, the solution is still blue, add more sugar solution and reboil. When no longer able to distinguish any residual copper by the eye, suck a few drops of the boiling hot liquid into an end reaction tube and test the filtrate for Cu with ferro-cyanide of potassium solution and acetic acid. If copper be still present, add the sugar solution little by little, boil, and retest until no copper is found. Having thus determined the approximate quantity of sugar solution to be used, repeat the test twice, adding at first each time almost the entire quantity of sugar solution necessary to complete reduction.

(*b*) *Gravimetric.*—Take 25 cubic centimeters of copper solution of following composition:

34.639 grams $CuSO_4 + 5H_2O$ in 500 cubic centimeters of water, add in Erlenmeyer flask 25 cubic centimeters of alkali solution made as follows:

173 grams Rochelle salts
51.6 grams NaOH
} in 500 cubic centimeters water.

Add 50 cubic centimeters of a sugar solution of such strength as to leave a part of the copper unreduced; heat quickly to boiling point and boil for exactly two minutes; add 100 cubic centimeters recently boiled, cold, distilled water. The liquid is poured at once into a filter tube made of hard glass with asbestos diaphragm (an ordinary extraction tube is well adapted for this purpose). The asbestos film should be previously moistened. Bring finally all the separated suboxide into the tube with the help of a feather brush, and wash with 300 to 400 cubic centimeters of boiling water; afterward with 20 cubic centimeters absolute alcohol, and finally with ether; then dry, heat to low redness to convert into oxide and to destroy any organic matter. The copper may also be weighed in the metallic state after reduction in a stream of dry hydrogen. The tube should in all cases be kept in a desiccator before weighing.

(*c*) (*Gravimetric.*)

Reagents:

34.639 grams $CuSO_4 + 5H_2O$
125.000 grams NaOH
173.000 grams Rochelle salts
} in 500 cubic centimeters.

Process.—In a beaker of 250 cubic centimeters capacity place 25 cubic centimeters each of the reagents and 50 cubic centimeters of water. Heat to boiling and add 25 cubic centimeters of the solution to be tested, which should contain about 1 per cent of reducing sugar (dextrose, levulose). Boil for exactly two minutes, decant into a Gooch crucible, wash by decantation with 100 cubic centimeters of boiling-hot water, keeping the cuprous oxide in the beaker constantly covered. Place the beaker containing the cuprous oxide in place of the one receiving the wash water and dissolve the Cu_2O in a Gooch crucible in a fine stream of HNO_3; wash until all $Cu(NO_3)_2$ is removed. Transfer the whole of the nitrate from the beaker to a tared platinum dish, add a little H_2SO_4, and evaporate over steam bath until all HNO_3 is expelled and the Cu is converted into $CuSO_4$; connect with battery of four gravity cells and allow electrolytic action to continue for three hours or until all the Cu is deposited. (Connect the dish with the zinc pole of the battery.) Pour off the acid solution, adding water until all trace of H_2SO_4 is removed; wash with 95 per cent alcohol and finally with absolute alcohol; ignite residual alcohol, cool in desiccator, and weigh; calculate sugar reduced from weight of metallic copper by the following factors:

(1) Multiply weight of copper by 0.5698 for weight of invert sugar.

(2) Multiply weight of copper by 0.5308 for weight of anhydrous dextrose.

These factors are correct only for a copper solution of above strength and reducing sugar of approximately 1 per cent strength.

Sucrose.—(Optical method, to be used when the sugar is approximately pure.)

(*a*) Dissolve 26.048 (for the Ventzke), (16.19 for the Laurent scale) grams of sugar in water at temperature at which the polarization is to be made, and, after clarification, make the volume up to 100 cubic centimeters. The sugar is conveniently weighed in a counterpoised nickel or German silver dish with large lip, whence it is readily washed into the flask. The solution before being filled to the mark is clarified by the addition of lead subacetate or phospho-tungstic acid until no further precipitation takes place. Excess of lead should be avoided. The filtration and clarification may often be helped by adding a few drops of suspended aluminic hydrate after the lead.

The flask is filled with pure water until the lower line of the meniscus coincides with the mark on the neck. The mouth of the flask is closed with the thumb and its contents well shaken, and poured into a folded filter; the first 15 to 20 cubic centimeters of the filtrate are rejected. The subsequent filtrate, if not perfectly clear, is returned to the filter, and this continued until the filtrate shows no cloudiness. A 200 (100 to 500) millimeter tube is filled with the solution, placed in the polariscope, the scale of which, after neutralizing the rotation produced by the sugar by turning the analytical prism or moving the quartz wedge, will give the percentage of sucrose in the sample taken. A dark solution may either be read in a 100-millimeter tube or the solution may be decolorized by shaking it with a small quantity of dry bone-black. A weak solution may be read in a tube from 300 to 500 millimeters in length.

(*b*) *Optical method by inversion.*—For raw sugars, molasses, etc.

(1) *Method of Clerget.*—Make up the solution as above and place 50 cubic centimeters of the filtrate in a flask marked at 50 and 55 cubic centimeters. Fill to upper mark with strong HCl and mix well; place in hot water and heat quickly to 68° C.; keep at this temperature for exactly ten minutes; remove, cool quickly to room temperature, and polarize, noting temperature. If the sample contained originally any invert sugar the second polarization should be made at approximately the same temperature as the first. The percentage of sucrose is then calculated by the following formula:

S = percentage of sucrose.
a = first polarization.
b = second polarization (usually to the left).
$a + b$ = sum of the polarizations.
t = temperature of observation in degrees C.

$$\text{then } S = \frac{a + b}{144 - \frac{t}{2}}$$

When b is to the left, a and b are to be added; when b is to the right, it is to be subtracted from a.

(2) *Method of Lindet.*—Place 50 cubic centimeters of the filtrate as above in a flask marked at 100.5 cubic centimeters; add 5 grams of powdered zinc (zinc dust), place in boiling water, and when at boiling point add, little by little, 5 cubic centimeters of strongest HCl. After the acid has all been added, cool and make up to mark. Polarize in a 400-millimeter tube, or multiply the reading in a 200-millimeter tube by 2. Calculate percentage of sucrose as before.

Gravimetric method.—Determine first any reducing sugar in sample by methods mentioned above; then invert sucrose, neutralize free acid, and redetermine the reducing sugar. Deduct the percentage of reducing sugar obtained at first, and the remainder will be reducing sugar derived from sucrose; multiply this number by 95 to obtain percentage of sucrose in sample.

LACTOSE (ANHYDROUS).

Take 20.56 grams (16.19 sucrose) or 32.99 grams (26.048 sucrose) dissolve, clarify if necessary, and complete volume to 100 cubic centimeters. The reading of the vernier scale of the instrument will give the true percentage of lactose. The lactose may also be determined by the alkaline copper method, 10 cubic centimeters standard Fehling solution is equal to .067 grams lactose. The weight of copper reduced multiplied by .7635 = lactose.

LACTOSE IN MILK.

The reagents, apparatus, and manipulation necessary to give the most reliable results in milk-sugar estimation are as follows:

Reagents.—(1) *Basic plumbic acetate,* specific gravity 1.97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One cubic centimeter of this will precipitate the albumens in 50 to 60 cubic centimeters of milk.

(2) *Acid mercuric nitrate.* Dissolve mercury in double its weight of nitric acid, specific gravity 1.42. Add to the solution an equal volume of water. One cubic centimeter of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarization.

(3) *Mercuric iodide with acetic acid.* KI 33.2 grams, $HgCl_2$ 13.5 grams, $C_2H_4O_2$ 20 cubic centimeters, H_2O 64 cubic centimeters.

Apparatus.—(1) Pipettes marked at 59.5, 60, and 60.5 cubic centimeters. (2) Sugar flasks marked at 102.4 cubic centimeters. (3) Filters, observation tubes, and polariscope. (4) Specific gravity spindle and cylinder. (5) Thermometers.

Manipulation.—(1) The room and milk should be kept at a constant temperature. It is not important that the temperature should be of any given degree. The work can be carried on equally well at 15° C., 20° C., or 25° C. The slight variations in rotary power within the above limits will not affect the result for analytical purposes. The temperature selected should be the one which is most easily kept constant.

(2) The specific gravity of the milk is determined. For general work this is done by a delicate specific gravity spindle. Where greater accuracy is required, use specific gravity flask.

(3) If the specific gravity be 1.026, or nearly so, measure out 60.5 cubic centimeters into the sugar flask. Add 1 cubic centimeter of mercuric nitrate solution, or 30 cubic centimeters mercuric iodide solution, and fill to 102.4 cubic centimeter mark. The precipitated albumen occupies a volume of about 2.44 cubic centimeters. Hence the milk solution is really 100 cubic centimeters. If the specific gravity is 1.030, use 60 cubic centimeters of milk. If specific gravity is 1.034, use 59.5 cubic centimeters of milk.

(4) Fill up to mark in 102.4 cubic centimeter flask, shake well, filter, and polarize.

NOTES.—In the above method of analysis the specific rotatary power of milk-sugar is taken at 52.5, and the weight of it in 100 cubic centimeter solution to read 100° in the cane sugar scale at 20.51 grams. This is for instruments requiring 16.19 grams sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk-sugar, whatever instrument is employed.

Since the quantity of milk taken is 3 times 20.51 grams, the polariscopic readings divided by 3 give at once the percentage of milk-sugar when a 200-millimeter tube is used.

If a 400-millimeter tube is employed, divide reading by 6; if a 500-millimeter tube is used, divide by 7.5.

Since it requires but little more time, it is advisable to make the analysis in duplicate and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102.4 for 60 cubic centimeters no correction for volume of precipitated casein need be made. In no case is it necessary to heat the sample before polarizing.

ELECTIVE METHODS.

1.

PLAN A.—DIRECTIONS FOR THE EXAMINATION OF SIRUPS WHICH CONTAIN 2 PER CENT OR MORE OF INVERT SUGAR, STARCH SUGAR, OR RAFFINOSE, AS ALSO OF SUGARS CONTAINING RAFFINOSE.

[Official German method used in taxing sugars.] *

In the examination of those sirups, which have been handed over to the chemist because they contain 2 per cent or more of invert sugar, the determination of the specific gravity and degree Brix can be made as directed in Article A. Naturally the direct determination of the specific gravity by means of the picnometer can take the place of this method, but in no case is it allowable to substitute the estimation of total solids, as on the one hand this would cause differences in the coefficient of purity as obtained by the officers and chemists, and on the other hand the determination of total solids in sirups containing invert sugar is much too difficult and takes up too much time to be of any use in every-day practice. In calculating the coefficient of purity the method used in the sugar-house, namely, considering only sucrose as sugar, can not be used, but the invert sugar must be calculated as sucrose by deducting one-twentieth of the amount found, adding to the direct content of sucrose and basing the calculation on this result.

For the determination of the sugar-content various methods can be applied according to the amount of invert sugar, starch sugar, or raffinose present. The following remarks will offer some explanation:

The invert sugar of sirups is very often inactive, but can nevertheless have the power of rotating to the left, which deviation according to late investigations is 0.33, according to others 0.34 times as great as the right-handed rotation of sucrose. Consequently, as soon as considerable invert sugar is present, the polarization of the sucrose present will be correspondingly diminished. As is well known Meissl proposed in the examination of colonial sugars to multiply the invert sugar found by 0.34, add this to the polarization, and thus arrive at the correct amount of sucrose. This method would, however, be out of place in the analysis of sirups, as the invert sugar present very often does not show its normal rotatory power, but varies down to complete inactivity. Meissl's correction in such cases would lead to unreliable results. At the same time the rotatory power of the invert sugar may cause the results to be too low. In considering all these circumstances it becomes obvious that the determination of total sugar from the polarization and the invert sugar found is only possible when the invert sugar present does not exceed a certain percentage. For instance, if 6 per cent of invert sugar were present the amount of sucrose could be $6 \times 0.33 = 1.98$ per cent too low. Therefore, as the sirups handed to the chemist for examination may contain considerable quantities of invert sugar whose rotatory power we do not know, we recommend the rejection of the optical method completely, and the adoption of a gravimetric one, a new and easy modification of which will be given under I.

The presence of starch sugar or raffinose makes a difference. The reducing power of starch sugar, which in the commercial article presents a variation corresponding to from 40 to 60 per cent of sugar, is not changed by the conditions under which the inversion of sugar sirups is made in the gravimetric method; and as we can not determine the quantity of starch sugar present accurately, the gravimetric method for the estimation of the total content of beet sugar and of the quotient of purity is no longer applicable. It would on the contrary lead to large errors, and sirups having a coefficient of purity of over 70 would, if examined by this method, after the addition of a certain quantity of starch sugar, appear to be below 70. In

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such cases, where starch sugar is present, the influence exerted by the laevo-rotation of the invert sugar upon the polarization can no more be considered, as starch sugar has a higher dextro-rotatory power than the other sugars present. To avoid mistakes, which could be easily caused by adding starch sugar to sirups of a coefficient of purity of over 70, it is best, when starch sugar is present, to calculate the real sucrose content from the polarization and the invert sugar directly determined. This method is described under II. If raffinose is present still another method, which will be found under III, must be adopted.

I.—*The presence of starch sugar need not be considered.*

The examination of sirups which do not contain any starch sugar sirup, will be a common occurrence, as such an addition is generally not made by the manufacturers themselves, but rather by the dealers. One operation will here suffice for the determination of total sugar.

Weigh out one-half the normal weight (13.024 grams) of sirup, dissolve in a 100 cubic centimeter flask in 75 cubic centimeters of water, add 5 cubic centimeters hydrochloric acid (38.8 per cent HCl), and warm in a water bath to 67° to 70° C. As soon as the contents of the flask have reached this temperature, heat for five minutes, not allowing the temperature to rise above 70° C., and shaking frequently. As the previous warming will take from two and a half to five minutes, the whole operation will require from seven and a half to ten minutes. Fill up to the mark, shake, and dilute 50 cubic centimeters of this solution to a liter. By means of a pipette transfer 25 cubic centimeters of this to a flask and add 25 cubic centimeters of a solution of sodium carbonate (1.70 grams anhydrous salt to the liter) to neutralize the free acid present. Add 50 cubic centimeters of Soxhlet's solution, heat to boiling, as in the determination of invert sugar, and keep the liquid in ebullition for three minutes. As all the sucrose in this solution has been inverted, and is therefore unable to influence the result, we need not be so careful about the time of boiling. Soxhlet's experiments show that two or three minutes difference will not influence the result materially. Dilute the liquid with an equal volume of water, which has been previously boiled so as to expel air, and continue as directed under the determination of invert sugar. The tables so far published for the calculation of results are of no value in this case, as they have been constructed with regard to glucose or a mixture of invert sugar and saccharose. The following table has been compiled for invert sugar and enables the analyst to calculate the amount of sucrose directly from the amount of copper found.

Table for calculating the sucrose corresponding to the invert sugar present from the copper found on three minutes' boiling.

Sucrose. Mg.	Copper. Mg.	Sucrose. Mg.	Copper. Mg.	Sucrose. Mg.	Copper. Mg.	Sucrose. Mg.	Copper. Mg.
40	79.0	73	145.2	106	208.6	139	269.1
41	81.0	74	147.1	107	210.5	140	270.9
42	83.0	75	149.1	108	212.3	141	272.7
43	85.2	76	151.0	109	214.2	142	274.5
44	87.2	77	153.0	110	216.1	143	276.3
45	89.2	78	155.0	111	217.9	144	278.1
46	91.2	79	156.9	112	219.8	145	279.9
47	93.3	80	158.9	113	221.6	146	281.6
48	95.3	81	160.8	114	223.5	147	283.4
49	97.3	82	162.8	115	225.3	148	285.2
50	99.3	83	164.7	116	227.2	149	286.9
51	101.3	84	166.6	117	229.0	150	288.8
52	103.3	85	168.6	118	230.9	151	290.5
53	105.3	86	170.5	119	232.8	152	292.3
54	107.3	87	172.4	120	234.6	153	294.0
55	109.4	88	174.3	121	236.4	154	295.7
56	111.4	89	176.3	122	238.3	155	297.5
57	113.4	90	178.2	123	240.2	156	299.2
58	115.4	91	180.1	124	242.0	157	300.9
59	117.4	92	182.0	125	243.9	158	302.6
60	119.5	93	183.9	126	245.7	159	304.4
61	121.5	94	185.8	127	247.5	160	306.1
62	123.5	95	187.8	128	249.3	161	307.8
63	125.4	96	189.7	129	251.2	162	309.5
64	127.4	97	191.6	130	252.9	163	311.3
65	129.4	98	193.5	131	254.7	164	313.0
66	131.4	99	195.4	132	256.5	165	314.7
67	133.4	100	197.3	133	258.3	166	316.4
68	135.3	101	199.2	134	260.1	167	318.1
69	137.3	102	201.1	135	261.9	168	319.9
70	139.3	103	202.9	136	263.7	169	321.6
71	141.3	104	204.8	137	265.5	170	323.3
72	143.2	105	206.7	138	267.3		

Example: 25 cubic centimeters of the solution = 0.1628 grams substance, gave 0.1628 grams of copper, which corresponds to 0.052 grams of sugar. Therefore the sirup contained 50.4 per cent sugar.

Supposing that this sirup showed 80° Brix, then its coefficient would be 63. This coefficient is only calculated to tenths, hundredths in the case of the degree Brix being taken as an additional tenth, while with the coefficient they are not considered, thus 82.85 Brix would be read 82.9, while a coefficient of 69.99 is taken as 69.9 and not 70.

II.—The sirup to be examined may contain starch sugar.

In this case a direct polarization must first be made. If this gives a coefficient of purity above 70, further examination is unnecessary, as it would only tend to raise the coefficient, never to lower it.

If, however, the coefficient falls below 70, the presence of starch sugar is still possible. To determine whether any is present the sirup is inverted as in I, and made up to the mark.

It is then decolorized by adding $\frac{1}{2}$ to 1, in the case of dark sirups from 2 to 3 grams of bone charcoal previously washed with hydrochloric acid or of charred blood. If the latter is used, its absorption factor for invert sugar must be previously determined, and a corresponding correction in the polarimetric reading made in case the left-handed rotation is to be estimated accurately. In the present case it is sufficient to approximately determine this rotation at about 20°. Experience has shown that unadulterated sirups do not always have a laevo-rotation corresponding to 0.33 of the original right-handed rotation, but in all cases it is at least one-fifth of the original reading. A sirup polarizing 55 directly should, after inversion, read at least —11, calculated for normal weight. If this sirup should read —10 or less, or should even rotate to the right, then it has been adulterated with starch sugar. When the absence of starch sugar has thus been proved the sirup must be examined according to I.

If, however, starch sugar is present, then we must arrive at the total sucrose by adding to the direct polarization the invert sugar found by Fehling's solution. In this procedure the Fehling's solution is used according to Soxhlet's directions, but as the amount of solution taken by this author would not suffice for 10 grams of substance, we have to make preliminary experiments to determine the quantity of sirup which should be taken. This is done most easily by diluting 10 grams sirup to 100 cubic centimeters, placing 5 cubic centimeters of Fehling's solution into several test tubes and adding successively 8, 6, 4, and 2 cubic centimeters of the sirup solution. Upon boiling we will arrive at a point where the Fehling's solution is no longer decolorized. If this is the case with 6 cubic centimeters then 6 grams of substance are weighed out, dissolved in 50 cubic centimeters of water, and 50 cubic centimeters of Fehling's solution added. The whole is boiled for two minutes and the analysis conducted as in the estimation of invert sugar.

The invert sugar is calculated according to Meissl's table. The following data concerning the use of the table are taken from the original article, Zeitschrift des Vereins für die Rübenzuckerindustrie des Deutschen Reiches, 1883, p. 768:

Let

I. $\frac{Cu}{2}$ = approximate absolute amount invert sugar = Z;

II. $Z \times \frac{100}{p}$ = approximate per cent invert sugar = y;

III. $\frac{100\ Pol.}{Pol. + y}$ = R, relative number for sucrose;

$100 - R = I$, relative number for invert sugar;

R : Z, relation of sucrose to invert sugar = 6;

IV. $\frac{Cu}{p} \times F$ = correct percentage of invert sugar.

In these formulas Cu is the weighed copper,

p the amount of substance taken,

Pol. the polarization,

Z facilitates reading the vertical column, and R : Z the horizontal column of the following table.

To use the table find the columns agreeing most closely with the values found for Z and R : Z. When these columns meet the value of factor F will be found.

Factors for the determination of invert sugar in the presence of sucrose.

Sucrose : invert sugar = R : Z.	Milligrammes invert sugar = Z.									Factors = F.
	245	225	200	175	150	125	100	75	50	
90 : 10	56.2	55.1	54.1	53.6	53.1	52.6	52.1	51.6	51.2	
91 : 9	56.2	55.1	54.1	53.6	52.6	52.1	51.6	51.2	50.7	
92 : 8	56.2	54.6	53.6	53.1	52.1	51.6	51.2	50.7	50.3	
93 : 7	55.7	54.1	53.6	53.1	52.1	51.2	50.7	50.3	49.8	
94 : 6	55.7	54.1	53.1	52.6	51.6	50.7	50.3	49.8	48.9	
95 : 5	55.7	53.6	52.6	52.1	51.2	50.3	49.4	48.9	48.5	
96 : 4	.....	.....	52.1	51.2	50.7	49.8	48.9	47.7	46.9	
97 : 3	.....	.....	50.7	50.3	49.8	48.9	47.7	46.2	45.1	
98 : 2	.....	.....	49.9	48.9	48.5	47.3	45.8	43.3	40.0	
99 : 1	.....	.....	47.7	47.3	46 5	45.1	43.3	41.2	38.1	

Example: The polarization of a sugar is 86.4 and 3.256 grams substance = p is equivalent to 0.290 grams copper = Cu, then:

I. $\frac{Cu}{2} = \frac{0.290}{2} = 0.145 = Z$;

II. $Z \times \frac{100}{p} = 0.145 \times \frac{100}{3.256} = 4.45 = y$;

III. $\frac{100 \times Pol.}{Pol. + y} = \frac{8640}{86.4 + 4.45} = 95.1 = R$;

$100 - R = 100 - 95.1 = Z$; $R : Z = 95.1 : 4.9$.

By consulting the table we find that column 150 comes nearest to Z = 145 and column 95 : 5 is nearest to R : Z = 92.1 : 4.9.

Where these columns meet we find the factor 51.2, which enters into the last calculation.

$$\text{IV.}\quad \frac{Cu}{p} \times F = \frac{0.290}{3.256} \times 51.2 = 4.56 \text{ per cent invert sugar.}$$

To convert this into saccharose, we subtract $\frac{1}{20}$; 4.56 — 0.23 = 4.33; add this figure to the direct polarization and calculate the coefficient of purity from this and the degree Brix.

III.—*The presence of raffinose must be considered.*

If the chemist is required to consider the presence of raffinose he must proceed as follows:

(*a*) The direct polarization of the sugar is determined, as also (*b*) the indirect polarization at exactly 20° C.

The same precautions must be taken in making the inversion as in I and II. Half the normal weight is dissolved in 75 cubic centimeters of water in a 100 cubic centimeter flask, 5 cubic centimeters hydrochloric acid (38.8 per cent HCl) added and heated for seven and one-half to ten minutes to 60 to 70° C. After making up to the mark and clarifying with washed bone-black, the reading is taken at exactly 20° C. The following formula serves to calculate the result:

$$Z \text{ (sugar)} = \frac{0.5188\,P - J}{0.845} \text{ and } R \text{ (raffinose)} = \frac{P - Z}{1.85},$$

when P = direct polarization and J = invert reading for normal weight, the prefixed sign having been changed.

The invert sugar is determined as in other sirups. If the test described in Article A shows it to be present in quantities of less than 2 per cent, then it need not be further considered. 2 per cent or more of invert sugar must be determined quantitatively according to Meissl's method described in II and calculated as saccharose. In finding the factor of this table, raffinose is to be considered as sucrose and Meissl's value. Pol. is therefore the sum of sucrose and raffinose. The coefficient of purity is calculated from the degree Brix and the total sucrose (that is sucrose + invert sugar calculated to sucrose), the raffinose not being considered.

Example: The examination of a sirup gave 85.6° Brix, 76.6 direct polarization, —3 Pol. after inversion. By using the above formula we find 50.5 sucrose and 14 raffinose. There were also found 2.1 per cent. sucrose as invert sugar. Therefore the total sucrose is 52 6 and the coefficient 61.4.

Rank deceptions might be practiced by adding small amounts of starch sugar sirup to very pure sirups and requesting an examination with regard to raffinose present. In such cases the above method would cause an error in finding too small a sugar content and a considerable amount of raffinose corresponding to the starch sugar added.

The application of this method for the examination of sirups supposed to contain raffinose is hence only possible when no starch sugar is present. If starch sugar is known to be present, then the method described in II must be used.

The estimation of starch sugar can not be made exactly as described in II for sirups in general, as sirups containing raffinose give a different invert reading.

If, therefore, a product is to be examined which is supposed to contain raffinose, it is best to use method No. III, and calculate sucrose and raffinose from this. The observed readings should not vary more than +5° from the calculated readings, otherwise starch sugar is certainly present and the raffinose formula no more applicable. In such a case the sirup must be examined according to II.

IV.—*Examination of sugars for raffinose.*

The method of examining sirups containing raffinose can be applied to sugars. The direct polarization is taken in the usual manner, the indirect after inversion of one-half the normal weight just as directed for sirups under III (*b*) and the content of sucrose and raffinose calculated by means of the formula given in III. Numerous experiments have shown this method to give reliable results. Thus there were found in mixtures of sucrose and raffinose:

Mixture.		Found by the method.	
Sucrose.	Raffinose.	Sucrose.	Raffinose.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
97.00	3.00	97.02	2.98
91.00	9.00	90.99	8.95
85.00	15.00	85.06	14.97

Though without doubt this method is very accurate, still a wide limit must be given for experimental errors on account of its novelty. A variation of 0.6 between the sucrose as calculated by the raffinose formula and that determined directly by polarization has therefore been made the limit. Supposing, for instance, that the sucrose found by direct polarization is 92.6 and that calculated by the formula 92 per cent, then we may suppose this difference to be caused by errors in the method. In such a case raffinose should be reported absent and the direct polarization used for the sugar content. If, however, only 91.9 per cent sucrose were found by the formula while the direct polarization was 92.6, then the presence of raffinose can not be doubted. To avoid mistakes which may be caused by larger errors than 0.6, it is advisable to make a control determination in all cases where the difference is less than 1 per cent, and to base the presence or absence of raffinose upon the result of this control.

The above limit for errors will not influence the utility of the method, as the percentage of raffinose so far observed in high sugars always corresponded to more than 0.6 per cent of sucrose. No method has yet been proposed for the determination of smaller amounts of raffinose and they may therefore be neglected. Scheibler's method of calculating small amounts of raffinose by supposing the organic substances not sugar to be equal to the ash is not accurate, as the excess of organic substance over ash is not known.

The method is, however, of value in cases where the result found by the formula varies comparatively little from the polarization; for instance, corresponding to less than 1 per cent of sucrose. Here it will decide whether raffinose is present or whether the difference is caused by errors.

For this purpose the polarization, moisture, and ash are determined, the organic substances not sugar taken as equal to the ash, and these four constituents added together. In all cases where raffinose is present the result will be over 100; if it falls below 100, raffinose may be considered absent. In the former case, the percentage of raffinose is calculated as follows:

The percentage of water plus twice the ash is deducted from 100.

The result corresponds to the percentage of sucrose plus anhydrous raffinose. If we substitute a for the figure thus found, p for the direct polarization, x for the sucrose present, and y for the raffinose present, then.

$$x + 1.85\,y = p$$

$$x + y = a$$

$$x\ (\%\ \text{sucrose}) = \frac{1.85\,a - p}{0.85}$$

$$y\ (\%\ \text{raffinose}) = \frac{a - 1.85\,a - p}{0.85.}$$

The limit for error must here be placed at 0.3; that is, the sum of polarization, twice the ash and moisture must be more than 100.3, if the method is employed. Otherwise the result would be too uncertain for practice, as errors of 0.2 may easily occur in the direct reading. The following example has been so constructed as to show that the method with the above limit of error is not capable of determining variations of 0.6 per cent.

A sugar gave 99.7 polarization, 0.4 water, and 0.1 ash; then the sum total was:

99.7	$a = 100.0$
$+$ 0.4	$-$ 0.4
$+ 2 \times 0.1 =$ 0.2	$-$ 0.2
100.3	$a = 99.4$ $p = 99.7$

Therefore x (sucrose) $= 99.05$, which is taken as 99.1, and y (raffinose) $= 0.3$. It is apparent that the 0.3 plus polarization, found by this method, and which must be taken as the limit of error, correspond exactly to the variation between actual sucrose and direct reading, which has been made the limit for the inversion method with raffinose formula. The control is unnecessary when a difference of 1 per cent or more is found between the actual sucrose and direct reading. Very often the result of the raffinose formula is taken even if the control gives a negative result. If Scheibler's method gives negative results with a sugar varying less than 1 per cent, then raffinose should be reported absent. If, however, the control leaves any doubt, as when the sum varies between 100 and 100.3, or if raffinose is actually found, then the results obtained by the inversion method should always be reported, as long as the difference between the sucrose found and the direct reading amounts to more than 0.6 per cent. If it is less than 0.6 or just 0.6, then the analyst should report that he is unable to detect raffinose. In calculating the final result hundredths should be taken as an additional tenth; thus, 97.01 per cent sucrose is 97.1.

Plan B.—Official Instructions for the Examination of Chocolate, Candies, and Liquors for the Quantity of Sucrose contained therein.

A. The examination, especially of chocolate, preserved fruits, and liquors, must be primarily directed toward the detection of starch sugar, or honey.

B. The Soleil-Ventzke saccharimeter is used in the sucrose determinations. The directions for the use of the instrument will be found in Plan C of the official bulletin published as an appendix to the sugar-tariff law of July 9, 1887.

Ventzke's scale is so arranged that a 200-millimeter tube filled with a sugar solution containing 26.048 grams per 100 cubic centimeters will read 100.

If 26.048 grams of a substance are weighed out, dissolved in 100 cubic centimeters of water and polarized in a 200-millimeter tube, the number of degrees read on the scale will be the per cent by weight of sugar in the material.

The same is the case when 13.024 grams are dissolved in 50 cubic centimeters. If this weight (one-half normal weight) has been dissolved in 100 cubic centimeters the reading of the polariscope must be doubled.

If any other quantity (p grams) was weighed out, dissolved in 100 cubic centimeters and polarized in the 200-millimeter tube, the number of degrees read on the scale (a) $\times$ 0.26048 will give the grams sucrose in 100 cubic centimeters of the solution, and

$$\frac{26.048 \cdot a}{p}$$

will give the per cent sucrose in the substance analyzed.

In all cases where the substance to be examined contains no other optically active bodies, the direct polarization will give accurate results. If such are present, as for instance glucose, invert sugar, maltose, dextrin, pectinous bodies, the application of the polariscope becomes uncertain, and only in a few cases, which will be given below, can somewhat reliable results be obtained.

As regards the preparation of the solutions the following must be remembered: Material which consists mostly of sucrose and leaves only a small residue on being

treated with water, can be weighed out in the dish, and the solution immediately transferred to the sugar flask. When the substance, however, contains much insoluble matter, the latter should not be washed into the flask, as the volume of the sugar solution in such a case would be less than 100 cubic centimeters. In this case the residue must be separated from the solution by filtration and washing. Generally the sugar solution is not quite transparent and must be treated with some clearing agent. The solutions serving this purpose are:

(1) Lead acetate, of which from 1 to 10 cubic centimeters are mixed with the solution and the latter filtered after standing from one-fourth to one-half an hour.

(2) Lead acetate with subsequent addition of alum or aluminum sulphate, the lead sulphate formed carrying down the foreign matter.

(3) Aluminum hydrate in the form of a thin paste, of which several cubic centimeters are shaken with the solution.

(4) Tannic acid to precipitate albuminous substances. This must be examined beforehand with regard to its optical activity.

(5) Charred blood or boneblack to remove coloring matter, $\frac{1}{2}$ to 1 gram, are added to the liquid.

In some cases this clearing is difficult and the method best adapted must be determined by previous experiments. For solutions prepared from candies the pasty aluminum hydrate is the best medium.

When, as it is often the case, invert sugar is present, the result of the direct polarization will be too low on account of the left-handed rotation of this sugar. In such a case Clerget's inversion method must be applied to find the correct per cent of sucrose. This is conducted as follows: 26.048 grams are dissolved in a sugar flask and the solution made up to 100 cubic centimeters; 50 cubic centimeters of this solution are transferred by means of a pipette to a 50 or 55 cubic centimeter flask, cleared and polarized, the reading being corrected for the extra 5 cubic centimeters. The liquid adhering to the pipette is washed into the 100 cubic centimeter flask containing the remaining 50 cubic centimeters (13.024 grams), 5 cubic centimeters of concentrated hydrochloric acid (38 per cent, specific gravity 1.88 at 15° C.) added and the flask heated for fifteen minutes at 67° to 70° C. in a water bath. The temperature should not exceed this limit. The flask is then cooled rapidly and the solution made up to 100 cubic centimeters. If the liquid is colored, it is shaken with $\frac{1}{2}$ to 1 gram of bone-black and filtered through a double filter. It is then polarized in a 200-millimeter tube which is provided with a thermometer. As the rotatory power of invert sugar is much influenced by the temperature, this factor must be regarded. The reading is best taken between 18° and 22° C. and the temperature accurately determined. The reading must also be doubled on account of the dilution of the liquid.

To calculate per cent of sucrose (R) the two readings are added together, the sum (S) multiplied by 100 and divided by $142.4 - \frac{1}{2}t$ where t is the temperature at which the invert reading was taken. If the temperature is exactly 20° C., the result can be made more accurate by substituting 142.66 for 142.4, thus:

$$R. = \frac{100\ S}{142.66 - \frac{20}{2}} = \frac{100\ S}{132.66} = 0.7538\ S.$$

If very much invert sugar is present, both the direct and indirect readings must be taken at the same temperature.

I.—*Chocolate.*

Weigh out in a German silver dish 13.024 grams of the rasped chocolate, moisten with alcohol (to aid the solution in water), add 30 cubic centimeters of water, and heat for ten to fifteen minutes on the water bath. Filter while warm into a 100 to 110 cubic centimeter flask, using a folded filter, any turbidity of the filtrate not being of any consequence. The residue on the filter is washed with hot water until the filtrate amounts to about 100 cubic centimeters. Five cubic centimeters of lead

acetate are then added, the liquid allowed to stand fifteen minutes, and a few drops of alum solution and some moist aluminum hydrate added. The liquid is then made up to 110 cubic centimeters, shaken well, and filtered through a folded filter. Slight moistening of the filter will aid filtration, but the first 25 cubic centimeters of filtrate should then be rejected. The polarization should be increased by one-tenth and then doubled.

II.—*Candies and confectionery.*

(*a*) *Dragees* (seeds or kernels coated with sugar and flour).— 26.048 grams are covered in a beaker with 40 to 50 cubic centimeters of water and allowed to stand, stirring now and then, until the mass is completely saturated. If the liquid shows an acid reaction, some precipitated calcium carbonate or a few drops of ammonia are added. The larger particles are now separated by filtering through cloth, the filtrate being collected in a 100 to 110 cubic centimeters flask. The residue on the filter is washed with cold water until about 100 cubic centimeters of filtrate have accumulated. Some aluminum hydrate is then added to clear it, the solution made up to 110 cubic centimeters with water, and about half a gram of bone-black added in case the liquid is colored. It is then allowed to stand half an hour, with occasional shaking. The solution is finally filtered through a dry folded filter.

A preliminary test for invert sugar is made with copper sulphate and soda lye, and the solution analyzed accordingly. Dragees almost always contain invert sugar.

(*b*) *Raffinade wafers* (cane sugar, with ethereal oils and coloring matter).— 26.048 grams dissolved in water, made up to 100 cubic centimeters in flask, and, if necessary, decolorized with bone-black. A preliminary test for invert sugar must always be made and the analysis directed accordingly.

(*c*) *Santonin wafers* (worm wafers, cane sugar, with santonin and some agglutinant, as egg albumen).— 13.024 grams dissolved in a 100 cubic centimeter flask (the santonin being insoluble), 5 cubic centimeters of lead acetate added, with a few drops of alum solution, the solution allowed to stand some time, with occasional shaking, made up to 100 cubic centimeters and filtered.

(*d*) *Dessert bonbons* (Fondant's, Pralinee's, chocolate bonbons, consisting of cane sugar or invert sugar, serving as a covering for marmalade, fruit, or chocolate).— 13.024 grams are treated with water and a few drops of ammonium hydrate until dissolved. If only a slight residue remains the whole can be immediately transferred to a 100 cubic centimeter flask, otherwise it must first be filtered. One-half of the liquid is inverted, the other polarized directly after having been cleared by means of aluminum hydrate in a 50 to 55 cubic centimeter flask.

(*e*) *Marzipan Masse* (cane sugar, with crushed almonds).— 13.024 grams material are triturated in a porcelain mortar with cold water, then mixed in a flask with 50 cubic centimeters of water and about 30 cubic centimeters of pasty aluminum hydrate, well shaken and filtered into a 200 cubic centimeter flask. The residue on the filter is washed with water until the filtrate amounts to 200 cubic centimeters. As this candy contains no invert sugar the solution can be polarized directly in the 200 millimeter tube, the reading being multiplied by 4 to correct for the dilution.

(*f*) *Cakes and sweetened pastry.*— 26.048 grams of the powdered material are mixed in a flask with about 75 cubic centimeters alcohol (85 to 90 per cent) and allowed to stand one-half hour in a warm place. It is then filtered through a fine cloth filter and the residue washed several times with alcohol. The filtrate is collected in a porcelain dish and heated on the water bath until the alcohol has all been driven off. One-half gram bone-black is then added and the solution filtered into a 100 cubic centimeter flask. 50 cubic centimeters are used for inversion, the remainder polarized directly.

(*g*) *Sugar-coated and preserved fruits* (marmalade, compots, jellies).— A considerable amount of invert sugar and pectinous bodies are always present. The aqueous solution of the latter has no rotatory power. If the material is solid in consistence, a crushed

or finely cut average sample must be prepared. 13.024 grams are then mixed with 30 to 50 cubic centimeters of water and a few drops of ammonium hydrate (to neutralize any free vegetable acids) and allowed to stand several hours. It is then passed through a cloth filter into a 100 or 200 cubic centimeter flask, the residue washed several times with hot water, and about 10 cubic centimeters of aluminum hydrate and one-half gram bone-black added to the filtrate. It is then shaken and made up to the mark. After filtering the filtrate is polarized according to Clerget's method.

Fruit jellies and marmalade are analyzed in a similar manner.

If the sucrose articles enumerated under II, g was calculated by the formula

$$R = \frac{100\,S}{142.4 - \frac{1}{2}t},$$

we would only obtain the percentage present at the time of analysis. The acids of the fruit have, however, converted a large amount of the cane sugar originally used into invert sugar. The original percentage of cane sugar, which is taken as a basis for taxation by the custom-house, can be calculated from the reading of the inverted solution. If this reading is referred to 26.048 grams material dissolved in 100 cubic centimeters and polarized in a 200 millimeter tube, we have the following relations if the above figure is called B:

A solution of 26.048 grams of cane sugar in 100 cubic centimeters has, after inversion, at the temperature $t°$ the left-handed rotation $42.4 - \frac{1}{2}\,t$. The amount of cane sugar corresponding to the observed polarization B can thus be calculated by the proportion:

$$42.4 - \tfrac{1}{2}\,t : 26.048 = B : \frac{26.048 \cdot B}{42.4 - \frac{1}{2}\,t}$$

and this is contained in 26.048 grams of the material used. Therefore the original percentage r of cane sugar can be calculated from the second proportion.

$$26.048 : \frac{26.048 \cdot B}{42.4 - \frac{1}{2}\,t} = 100 : r$$

whence

$$r = \frac{100\,B}{42.4 - \frac{1}{2}\,t}$$

If 13.024 grams substance were used and the solutions polarized at exactly 20° C., then the following formula is more accurate:

$$r = \frac{100\,B}{42.66 - 10} = 3.062\,B.$$

III.—*Liquors.*

The percentage of sugar in liquors is generally expressed as grams per liter.

Every liquor must be previously tested for invert sugar by diluting a little in a test tube with water, adding five drops of copper sulphate solution and enough sodium hydrate to form a clear blue liquid. If no change occurs upon heating, cane sugar only is present; a yellow or red precipitate indicates the presence of other sugars.

Liquors which do not contain invert sugar may be polarized directly in the 200 millimeter tube, being previously decolorized with bone-black if necessary. If a high percentage of sugar is present, the polarization must be made in the 100 millimeter tube.

The presence of alcohol has no influence on the reading. The ethereal oils which are present, although optically active, are present in such small quantities as to be without influence. The grams per liter (R) are found, when A is the reading in a 200 millimeter tube, by: $R = 2.6048\,A$.

When invert sugar is present, the alcohol must be removed, as it materially changes the rotation of this sugar.

Fifty cubic centimeters of liquor are measured into a porcelain dish and evaporated to about one-half the volume on a water bath. If the liquid has an acid reaction, a few drops of ammonium hydrate must be added before heating it. The residue is washed into a 100 cubic centimeter flask and made up to the mark with water. One-half is then polarized directly, the other after inversion. Both solutions may have to be decolorized with bone-black.

Supposing

V = number of cubic centimeters used for analysis,
A = direct reading,
B = reading of inverted solution (both read in 200 millimeter tube),
t = temperature of inverted solution when polarized;

then the grams of cane sugar (R) in a liter may be calculated from the formula:

$$R = \frac{26.048\,(A - B)}{(142.4 - \frac{1}{2}\,t)\,V},$$

where, when the direct reading was +, the inverted reading —, the difference A — B becomes A + B.

If the temperature was exactly 20° C.,

$$R = 196.7\frac{A + B}{V}, \text{ or more accurately} = 196.35\frac{A + B}{V}$$

In liquors, as under III, *b*, the addition of the fruit juices may have caused inversion of a part of the cane sugar originally added. The original percentage of cane sugar is then calculated from the inverted reading just as for candied fruits. The grams of cane sugar (r) per liter are found from:

$$r = \frac{26.048\,B}{(42.4 - \frac{1}{2}\,t)\,V},$$

or when $t = 20°$,

$$r = 804\frac{B}{V} \text{ or more accurately} = \frac{26.048\,B}{32.66\,V} = 797.55\frac{B}{V}.$$

PLAN C.—DIRECTIONS FOR DETERMINING THE BONIFICATIOUS VALUE OF INVERT SUGAR SIRUP.

While the sirup is being barreled a number of samples are taken so as to obtain a good average. This is well mixed and 250 grams weighed out in a tared beaker. After dissolving in distilled water the beaker is placed on the balance and enough water added to bring the weight of sirup and water up to 1000 grams. The sirup has then been diluted with three times its weight of water. The solution is again well mixed with a glass rod and poured into a high cylinder. A special spindle is used to determine the percentage of invert sugar. This spindle is used similarly to the Brix spindle for analyzing sirups. It is graduated at 17½° C., and the following table is used to correct for the temperature:

Subtract from the reading.		Add to the reading.		Add to the reading.	
At 10° C.	0.35° Brix.	At 18° C.	0.03° Brix.	At 25° C.	0.50° Brix.
11° C.	0.29° Brix.	19° C.	0.09° Brix.	26° C.	0.57° Brix.
12° C.	0.25° Brix.	20° C.	0.17° Brix.	27° C.	0.64° Brix.
13° C.	0.22° Brix.	21° C.	0.24° Brix.	29° C.	0.71° Brix.
14° C.	0.18° Brix.	22° C.	0.31° Brix.	29° C.	0.79° Brix.
15° C.	0.14° Brix.	23° C.	0.38° Brix.	30° C.	0.87° Brix.
16° C.	0.10° Brix.	24° C.	0.44° Brix.		
17° C.	0.04° Brix.				

The reading is multiplied by 4 to obtain the per cent of invert sugar in the undiluted sirup. Hundreths are always read as an additional tenth.

Example: The spindle read 18.1 per cent invert sugar at 20°. Hence 0.17° must be added to the reading and the sum multiplied by 4.

$$18.1 + 0.17 = 18.27 \times 4 = 73.08, \text{ or } 73.10.$$

The weight of the cane sugar used in the preparation of the sirup is then calculated by subtracting $\frac{1}{20}$ and multiplying the result by the weight of the invert-sugar sirup.

METHODS FOR DETERMINING PHOSPHORIC ACID AND MOISTURE.

(1) *Preparation of sample.*—The sample should be well intermixed and properly prepared and passed through a sieve having circular perforations one twenty-fifth of an inch in diameter, so that separate portions shall accurately represent the substance under examination, without loss or gain of moisture.

(2) *Determination of moisture.*—(*a*) In potash salts, nitrate of soda, and sulphate of ammonia heat 1 to 5 grams at 130° C. till the weight is constant, and reckon water from the loss. (*b*) In all other fertilizers heat 2 grams, or if the sample is too coarse to secure uniform lots of 2 grams each, 5 grams, for five hours at 100° C. in a steam bath.

(3) *Water-soluble phosphoric acid.*—Weigh out 2 grams in a small beaker, wash by decantation four or five times with not more than from 10 to 15 cubic centimeters of water, then rub it up in the beaker with a rubber-tipped pestle to a homogeneous paste, and then wash four or five times by decantation with from 10 to 15 cubic centimeters of water. Transfer the residue to a 9 centimeter, No. 589 Schleicher and Schüll filter, and wash with water until the filtrate measures not less than 250 cubic centimeters. Mix the washings. Take an aliquot (corresponding to one-half gram) and determine phosphoric acid, as under total phosphoric acid.

(4) *Citrate-insoluble phosphoric acid.*—Wash the residue of the treatment with water into a 200 cubic centimeter flask with 100 cubic centimeters of strictly neutral ammonium citrate solution of 1.09 density, prepared as hereafter directed. Cork the flask securely and place it in a water bath, the water of which stands at 65° C. (The water bath should be of such a size that the introduction of the cold flask or flasks shall not cause a reduction of the temperature of the bath of more than 2° C.) Raising the temperature as rapidly as practicable to 65° C., which is subsequently maintained, digest for thirty minutes from the instant of insertion, shaking every five minutes, filter the warm solution quickly (best with filter pump), and wash with water of about the temperature of 65°. Transfer the filter and its contents to a capsule, ignite until the organic matter is destroyed, treat with 10 to 15 cubic centimeters of concentrated hydrochloric or nitric acid, digest over a low flame until the phosphate is dissolved, dilute to 200 cubic centimeters, mix, pass through a dry filter, take an aliquot and determine phosphoric acid as under total.

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods, it is to be made by treating 2 grams of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, etc.), the residue insoluble in ammonium citrate is to be treated by one of the processes described below.

(5) *Total phosphoric acid.*—Weigh 2 grams and treat by one of the following methods: (1) Evaporation with 5 cubic centimeters magnesium nitrate, ignition, and solution in acid. This method is to be used in case of all fertilizers containing cotton-seed meal. (2) Solution in 30 cubic centimeters concentrated nitric acid with a small quantity of hydrochloric acid. (3) Add 30 cubic centimeters concentrated hydrochloric acid, heat, and add cautiously in small quantities at a time about 0.5 gram of finely pulverized potassium chlorate.

Boil gently until all phosphates are dissolved and all organic matter destroyed; dilute to 200 cubic centimeters; mix and pass through a dry filter; take 50 cubic

centimeters of filtrate; neutralize with ammonia (in case hydrochloric acid has been used as a solvent add about 15 grams dry ammonium nitrate or its equivalent). To the hot solutions for every decigram of P_2O_5 that is present, add 50 cubic centimeters of molybdic solution. Digest at about 65° C. for one hour, filter and wash with water or ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution.) Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 cubic centimeters. Nearly neutralize with hydrochloric acid, cool, and add magnesia mixture from a burette; add slowly (one drop per second), stirring vigorously. After fifteen minutes add 30 cubic centimeters of ammonia solution of density 0.95. Let stand several hours (two hours is usually enough). Filter, wash with dilute ammonia, ignite intensely for ten minutes, and weigh.

(6) *Citrate-soluble phosphoric acid.*—The sum of the water-soluble and citric-insoluble subtracted from the total gives the citrate-soluble.

PREPARATION OF REAGENTS.

(1) *To prepare ammonium citrate solution.*—Mix 370 grams of commercial citric acid with 1,500 cubic centimeters of water; nearly neutralize with crushed commercial carbonate of ammonia; heat to expel the carbonic acid; cool; add ammonia until exactly neutral (testing by saturated alcoholic solution of coralline) and bring to volume of two liters. Test the specific gravity, which should be 1.09 at 20° C., before using.

(2) *To prepare molybdic solution.*—Dissolve 100 grams of molybdic acid in 400 grams or 417 cubic centimeters of ammonia of specific gravity 0.96, and pour the solution thus obtained into 1,500 grams or 1,250 cubic centimeters of nitric acid of specific gravity 1.20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phospho-molybdate. Decant the solution from any sediment, and preserve in glass stoppered vessels.

(3) *To prepare ammonium nitrate solution.*—Dissolve 200 grams of commercial ammonium nitrate in water and bring to a volume of 2 liters.

(4) *To prepare magnesia mixture.*—Dissolve 22 grams of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina and phosphoric acid; filter; add 280 grams of ammonium chloride, 700 cubic centimeters of ammonia of specific gravity 0.96, and water enough to make the volume of 2 liters. Instead of the solution of 22 grams of calcined magnesia 110 grams of crystallized magnesium chloride ($MgCl_2 + 6H_2O$) may be used.

(5) *Dilute ammonia for washing.*—One volume ammonia of specific gravity 0.96 mixed with three volumes of water, or usually one volume of concentrated ammonia with six volumes of water.

(6) *Nitrate of magnesia.*—Dissolve 320 grams of calcined magnesia in nitric acid, avoiding an excess of the latter; then add a little calcined magnesia in excess; boil; filter from excess of magnesia, ferric oxide, etc., and bring to volume of 2 liters.

METHODS OF ANALYSIS OF FERMENTED LIQUORS.

I. *Specific gravity.*—This determination is made with a pycnometer or a Westphal balance controlled by a pycnometer. Temperature 25° C.

II. *Alcohol.*—One hundred cubic centimeters of wine at 25° C. distilled (preferably in glass) give + cubic centimeter alcohol.

III. *Extract.*—Fifty cubic centimeters of wine (at 25° C.), in case of sweet wines a less amount, are evaporated in a platinum dish on the water bath to the proper consistency and then dried in a drying oven at 100° C. to constant loss of weight. Constant loss of weight is assumed when three weighings with equal intervals between the first and second and second and third give equal differences between the successive weighings. Weighings are to be made at intervals of fifteen minutes.

[NOTE ON THE EXTRACT DETERMINATION.—So far as I am aware no satisfactory method has been given for the determination of the extract of wine. I think that the method of the Bavarian chemists is on the whole the best. As the object is for purpose of comparison with some standard, we can not do better I think than to follow the standard most generally adopted. I have in mind when the new chemical laboratory of the University of California is fitted up to make some experiments on the determination of this extract in a vacuum at a moderate temperature. I should modify somewhat the method of Gautier. However, until some better method has been established, I believe the method given will be most satisfactory.]

IV. *Acidity* (total acid constituents of the wine expressed as tartaric acid).—If carbonic acid is present, expel by shaking. Titrate with dilute alkali solution. The neutral point is determined by adding a drop of solution to delicate litmus paper.

V. *Volatile acids* (expressed as acetic acid).—Distil in a current of steam and titrate the carefully condensed distillate with standard alkali (decinormal).

VI. *Glycerine.*—(1) This is determined in dry wines as follows: The alcohol is driven off from 100 cubic centimeters wine, lime or magnesia added, and the same evaporated to dryness. The residue is boiled with 90 per cent alcohol, filtered, and the filtrate evaporated to dryness. This residue is dissolved in 10 to 20 cubic centimeters alcohol, 15 to 30 cubic centimeters ether added, and the mixture allowed to stand until it is clear. It is then decanted from the sticky precipitate into a glass-stoppered weighing bottle, evaporated to constant loss of weight, and weighed.

(2) The following method is employed for sweet wines: One hundred cubic centimeters wine are measured into a porcelain dish and evaporated on the water bath to a sirupy consistence, mixed with 100 to 150 cubic centimeters absolute alcohol, poured into a flask, ether added in the proportion of 1½ volumes to each volume of alcohol used, the flask well shaken, and allowed to stand until the liquid becomes clear. This is then poured off and the residue again treated with a mixture of alcohol and ether. The liquids are mixed, the alcohol and ether driven off, the residue dissolved in water, and treated as in (1).

(3) In all glycerine determinations it is necessary to take into consideration the loss of glycerine due to its volatility with water and alcohol vapor, and accordingly to add to the glycerine found 0.100 gram for each 100 cubic centimeters of liquid evaporated.

(4) It is necessary to test the glycerine from sweet wines for sugar, and if any is present it must be estimated by Soxhlet's or Knapp's method and its weight subtracted from that of the glycerine.

VII. *Sugar.*—This is to be determined by Sohxlet's or Knapp's method. The presence of unfermented cane sugar is to be shown by inversion, etc.

Polarization.—(1) The wine is decolorized with plumbic subacetate.

(2) A slight excess of sodic carbonate is added to the filtrate from (1). 2 cubic centimeters of a solution of plumbic subacetate are added to 40 cubic centimeters white wine and 5 cubic centimeters to 40 cubic centimeters red wine, the solution is filtered and 1 cubic centimeter of a saturated solution of sodic carbonate added to 21.0 or 22.5 cubic centimeters of the filtrate.

(3) The kind of apparatus used and the length of the tube are to be given, and results estimated in equivalents of Wild's polaristrobometer with 200 millimeter tubes.

(4) All samples rotating more than 0.5 degree to the right (in 220 millimeter tubes, after treating as above), and showing no change or but little change in their rotatory power after inversion, are to be considered as containing unfermented glucose (starch sugar) residue.

(5) Rotatory power of less than 0.3 degree to the right shows that impure glucose has not been added.

(6) Wines rotating between 0.3 degree and 0.5 degree to the right must be treated by the alcohol method.

(7) Wines rotating strongly to the left must be fermented and their optical properties then examined.

VIII. *Tannin.*—Determine with Neubauer's permanganate method.

IX. *Potassic bitartrate.*—The determination of potassic bitartrate as such is to be omitted.

X. *Tartaric, malic, and succinic acids.*—(1) According to Schmidt and Hiepe's method.

(2) Determination of tartaric acid according to the modified Berthelot-Fleury method.

(3) If the addition of 1 gram finely powdered tartaric acid to 100 grams wine produces no precipitate of potassic bitartrate, the modified Berthelot-Fleury method must be employed to determine free tartaric acid.

XI. *Coloring matter.*—(1) Only aniline dyes are to be looked for.

(2) Special attention is to be paid to the spectroscopic behavior of rosaniline dyes as obtained by shaking wines with amylic alcohol before and after saturation with ammonia.

XII. *Inorganic matter* (ash).—Burn in ordinary manner in flat platinum dish at as low a heat as possible; repeated moistening, drying, and heating to redness are advisable to get rid of all organic substances.

XIII. *Citric acid.*—Presence to be shown by a qualitative test, as baric citrate.

XIV. *Sulphuric acid.*—To be determined in the wine after adding hydrochloric acid.

XV. *Chlorine.*—To be determined in the nitric acid solution of the burnt residue by Volhard's method.

XVI. *Lime, magnesia, and phosphoric acid.*—These are determined in the ash fused with sodic hydrate and potassic nitrate, the phosphoric acid by the molybdenum method.

XVII. *Potash.*—Either in the wine ash, as the platinum double salt, or in the wine itself, by Kayser's method.

XVIII. *Gums.*—Presence shown by precipitation by alcohol; 4 cubic centimeters wine and 10 cubic-centimeters 96 per cent alcohol are mixed. If gum arabic has been added, a lumpy, thick, stringy precipitate is produced; whereas pure wine becomes at first opalescent and then floculent.

XIX. *Sulphurous acid.*—One hundred cubic centimeters of wine are distilled in a current of carbonic acid after the addition of phosphoric acid. The distillate carefully condensed is oxidized with bromine and the amount of H_2SO_4 determined.

ABNORMAL CONSTITUTUENTS OF WINES.

Mannite.—When present in any considerable quantity it can be detected by simply allowing the wine (a few drops will be sufficient) to evaporate spontaneously upon a glass slide or plate. The mannite will crystallize in a characteristic stellated form, which can be recognized at a glance. It should be allowed to stand twenty-four to forty-eight hours. When the quantity is small extract the residue evaporated nearly or quite to dryness with boiling 80 per cent alcohol. Evaporate this extract to dryness and extract with 95 per cent boiling alcohol; the mannite if present in any quantity will separate out in part upon cooling. If allowed to evaporate spontaneously the characteristic stellated crystals can be obtained.

Lactic acid.—This will be found in the alcohol ether extract of evaporated residue and can be recognized by usual tests. It may be determined by titration with standard alkali. It may be necessary to take larger quantities of the wine for this investigation.

In diseased wines butyric acid may be tested for in the portion of volatile acid.

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